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<p>(21) International Application Number: PCT/US94/06699  (22) International Filing Date: 9 June 1994 (09.06.94)  (30) Priority Data: 074,136 9 June 1993 (09.06.93) US 074,312 9 June 1993 (09.06.93) US 074,313 9 June 1993 (09.06.93) US 074,314 9 June 1993 (09.06.93) US  (71) Applicant: LONZA INC. [US/US]; 17-17 Route 208, Fair Lawn, NJ 07410 (US).  (72) Inventor: WALKER, Leigh; 4758 Macungie Mountain Road, Macungie, PA 18062 (US).  (74) Agents: ROBINSON, Joseph, R. et al.; Darby &amp; Darby, 805 3rd Avenue, New York, NY 10022 (US).</p>	<p>(81) Designated States: AT, AU, BB, BG, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KG, KP, KR, KZ, LK, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, RO, RU, SD, SE, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: QUATERNARY AMMONIUM AND WATERPROOFING/PRESERVATIVE COMPOSITIONS  (57) Abstract  Quaternary ammonium compounds, compositions incorporating such compounds and waterproofers are provided.</p>		

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QUATERNARY AMMONIUM AND  
WATERPROOFING/PRESERVATIVE COMPOSITIONS

FIELD OF THE INVENTION

This invention relates to the preparation of  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl,  $C_8$ - $C_{20}$  alkyl quaternary ammonium hydroxide compositions (hydroxide quats) by an indirect synthesis method which uses a corresponding quaternary ammonium chloride as a starting material. Di  $C_8$ - $C_{12}$  alkyl quaternary ammonium hydroxides are useful in wood preservative systems, as surfactants, and as biocides. Preferably, these wood preservative systems are metal free.

This invention also relates to the indirect synthesis of  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl,  $C_8$ - $C_{20}$  alkyl quaternary ammonium carbonate compositions (carbonate quats) from corresponding quaternary ammonium chlorides. Di  $C_8$ - $C_{12}$  alkyl quaternary carbonate compositions are particularly useful in wood preservative systems, as surfactants and as biocides.

This invention further relates to di  $C_8$ - $C_{12}$  alkyl quaternary ammonium carboxylate(s) (carboxylate quat(s)) and di  $C_8$ - $C_{12}$  alkyl quaternary ammonium borate(s) (borate quat(s)) which are useful in metal-free wood preservative systems, as surfactants, and as biocides. These wood preservative systems are leaching resistant. Additionally, this invention relates to the synthesis of  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl,  $C_8$ - $C_{20}$  alkyl carboxylate or borate quats from corresponding quaternary ammonium chlorides.

Additionally, this invention relates to waterproofing and wood preservation compositions. Polyhydroxyl or polyether hydroxyl esters of fatty acids and polyether hydroxides have been found to be useful as waterproofers for wood substrates.

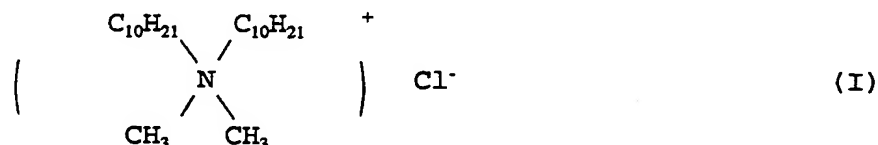
5 Furthermore, these waterproofers in combination with quaternary ammonium compositions and a solvent are useful as waterproofing wood preservation compositions. Preferred quaternary ammonium compositions include C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium chlorides, hydroxides, carbonates, carboxylates, or borates.

#### BACKGROUND OF THE INVENTION

Quaternary ammonium compounds (quats), and particularly didecyldimethylammonium chloride (DDAC)

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20



are commonly used as wood preservatives because they possess resistance properties to fungi and termites, to loss of strength, and to electrical sensitivity similar to those of commonly used acidic copper/chromium/arsenic solution (CCA) or ammoniacal copper and arsenic salt solution preservatives. See Proc of the Am. Wood Pres. Assoc., 80:191-210 (1984). Although chloride quats do not include potentially dangerous heavy metals, didecyldimethylammonium chloride leaches rapidly in soil (Nicholas et al., Forest Prod. J., 41:41 (1991), and therefore, does require coupling with copper salt.

Findlay et al., U.S. Patent No. 4,929,454, disclose a method of preserving wood by impregnation with a quaternary ammonium compound and at least one of zinc and copper, wherein the quat anion is chosen from the group consisting of hydroxide, chloride, bromide, nitrate, bisulfate, acetate, bicarbonate, and carbonate, formate, borate and fatty acids. These

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quats have distinct environmental and safety advantages over commonly used acidic copper/chromium/arsenic solution (CCA) or ammoniacal copper and arsenic salt solution preservatives in that potentially dangerous heavy metals are not included. The  
5 Findlay et al. quats require copper or zinc in order to render them relatively insoluble and to prevent them from leaching out of a treated substrate. The use of copper or zinc in the above formulations may yet raise environmental and corrosion concerns.

10 Additionally, didecyldimethylammonium chloride tends to absorb preferentially to the surface of the wood and does not uniformly treat the whole substrate. Finally, DDAC treated wood shows a surface erosion or ages upon exposure to light. See Preston et al., Proc. Am. Wood Pres. Assoc., 83:331 (1987).

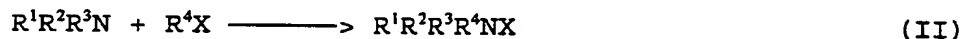
15 The biocidal activities of various chloride quats against bacteria, fungi, and algae are tabulated in Cationic Surfactants, E. Jungerman Ed., pp. 56-57, Marcel Dekker, Inc., 1969. Nicholas, "Interaction of Preservatives with Wood," Chemistry of Solid Wood, Advances in Chemistry Series #207,  
20 Powell ed., (A.C.S. 1984), notes that didecyldimethylammonium compounds and particularly DDAC are potential biocides. Preston, J.A.O.C.S. 60:567 (1983), concurs and suggests that maximum fungitoxicity is exhibited with dialkyldimethyl compounds having C<sub>10</sub>-C<sub>12</sub> alkyl groups. Butcher et al., Chem Abstracts No. 91:152627b, suggest that the presence of an acid or  
25 a base can affect the activity of didecyldimethylammonium quats.

Didecyldimethylammonium acetate was used as a phase transfer catalyst for an oxidation in Chem Abstracts No.  
30 97:9175. A wood preservative was prepared by autoclaving didecylmethyamine with gluconic acid and ethylene oxide in isopropanol to yield  $(C_{10}H_{21})_2 CH_3N (CH_2)_2O$  + gluconate in Chem Abstracts No. 109:124403x, while disinfectant solutions were prepared by exchanging a benzylammonium chloride with a chlor-  
35 hexidene gluconate in Chem Abstracts No. 103:109954f.

Microbiocidal compositions which include quaternary ammonium compounds of the formula  $R^1N^+R^2R^3R^4 X^-$ , wherein at least one of  $R^1$ ,  $R^2$ , or  $R^3$  is a  $C_8$ - $C_{30}$  alkyl or alkenyl group and the remainder of  $R^1$ ,  $R^2$  or  $R^3$  is methyl, ethyl,  $CH_2Ph$  or 4-pyridyl-methyl;  $R^4$  is methyl or ethyl; and  $X$  is an anion of an acid having a  $C_7$  or greater hydrophobic group, were disclosed in Chem Abstracts Nos. 113:154360f and 113:153776j. Chem Abstracts No. 112:79768u discloses compounds of the formula  $R^1R^2R^3R^4N^+X^-$ , wherein  $R^1$ ,  $R^2$ , and  $R^3$  are methyl, ethyl, benzoyl, 4-pyridinomethyl and at least one is  $C_8$ - $C_{30}$  alkyl or alkenyl;  $R^4$  is methyl or ethyl; and  $X$  is a counter anion of acids having  $C_7$  or greater hydrophobic groups. Dimethyldidecylammonium dodecylbenzenesulfonate was demonstrated to impart long term rot resistance to wood without causing rust, while the chloride salts of similar compounds were demonstrated to cause rust.

Patton et al., U.S. Patent No. 5,004,760, disclose polymeric foams incorporating various dialkyldimethylammonium carboxylates such as didecyldimethylammonium poly(ethylene/acetate) and the like.

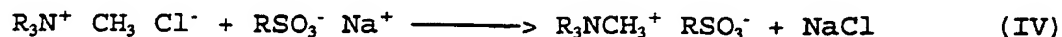
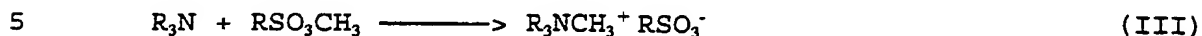
Quaternary ammonium compounds (quats) are typically prepared by the reaction:



wherein  $X$  is a halogen, a sulfate, a sulfo compound, or the like. When at least one of  $R^1$ ,  $R^2$ ,  $R^3$ , or  $R^4$  is  $C_{12}$  or longer, the product is an inert soap. Many of the inert soaps have biocidal activity against bacteria, fungi, algae, and related organisms.

Reaction (II) above is limited by the reactant  $R^4X$  because  $R^4$  must react with tertiary amines. For example, methyl chloride ( $R^4X = CH_3Cl$ ) will react with a tertiary amine at less than  $100^\circ C$  to yield a quaternary compound  $R_3N^+CH_3 Cl^-$ , while methanol or methyl acetate ( $R^4X = CH_3OH$  or  $CH_3COOCH_3$ ) will not, under similar reaction conditions.

General quaternary ammonium compounds with a sulfo group are easily prepared either by the reaction of a sulfate compound with a tertiary amine (III) or by a double exchange (IV).

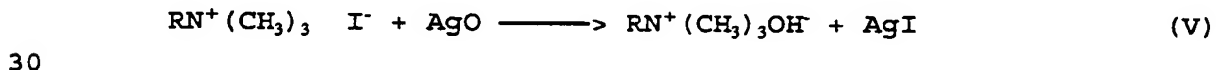


If trimethylamine is heated with carbon dioxide and methanol above 200°C and at 85 to 95 atmospheres, the carbonate quat, bis-tetramethylammonium carbonate, is prepared. Industrial Organic Nitrogen Compounds, Astle Ed. p 66, Reinhold Inc, 1961. However, this reaction is limited to the methyl compound because higher homologs decompose to olefins by the Hofman elimination reaction. See, Organic Reactions, 11, Chptr. 5, 377, Krieger Publishing Co., 1975.

Chem Abstracts 110:212114 (1989) suggests that dimethyl carbonate will react with triethylamine in methanol in twelve hours at 115°C and under pressure to yield a methyl carbonate ester quat.

Chem Abstracts 114:24824 (1991) discloses that 6-hydroxylhexyldimethylamine reacts with dimethyl carbonate to yield a carbonate ester quat.

Quaternary ammonium hydroxides (hydroxy quats), an intermediate in the reaction scheme of the present invention, are currently prepared by the reaction of quaternary ammonium iodide with silver oxide (V).



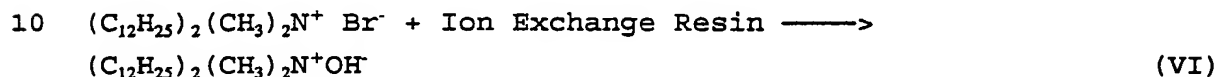
However, this reaction is costly, and it is difficult to recover the silver reagent. See, Organic Reactions, 11:Chptr 5, pp. 376-377, Krieger Publishing Co., 1975.

In an olefin synthesis, it has been suggested to treat a quaternary salt with aqueous sodium or potassium

followed by pyrolysis in order to form the hydroxy quat and then to decompose the hydroxy quat directly. However, in this method the hydroxy quat is not isolated and the conditions for its preparation are undesirable. See, Organic Reactions,

5 11:Chptr 5, pp. 376-377, Krieger Publishing Co., 1975.

Talmon et al., Science, 221, 1047 (1983), have used an ion exchange resin to convert didecyldimethylammonium bromide to didecyldimethylammonium hydroxide (VI).



However, 50 ml of ion exchange resin and two treatment steps were required to convert 3 grams of quaternary ammonium chloride to the corresponding hydroxide. Talmon et al. state that the hydroxy quat can be reacted with acids to make quats with different anions, and they have prepared didodecyldimethylammonium (DDDA) acetate, DDDA-formate, DDDA-propionate, DDDA-butylate, DDDA-oxalate, DDDA-acrylate, DDDA-tartrate, DDDA-benzoate, and DDDA-octanoate. See also, Organic Synthesis, Collective Volume VI, 552, John Wiley Inc., 1988; Brady et al., J. Am. Chem. Soc., 106:4280-4282, 1984; Brady et al., J. Phys. Chem., 90:9, 1853-1859, 1986; Miller et al., J. Phys. Chem., 91:1, 323-325, 1989; Radlinske et al., Colloids and Surfaces, 25 46:213-230, 1990.

Distearyldimethylammonium gluconate was prepared via ion exchange and subsequent reaction with an organic acid in Chem Abstracts No. 75:119170U. Miller et al, Langmuir, 4:1363 (1988) prepared ditetradecyldimethylammonium acetate by ion exchange from a bromide.

Alternatively, quaternary ammonium hydroxide compositions have been prepared by treating a haloquat in an electrochemical cell with special cation exchange diaphragms between the cells. The hydroxy quat collects at one electrode, and the halide collects at the other. Hydroxy quats,  $R^1R^2R^3R^4N^+OH^-$ ,

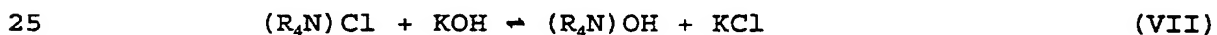
wherein the R groups were C<sub>1</sub>-C<sub>4</sub>, were treated with carboxylic acids to make asymmetric quats that were used as capacitor driving electrolytes. See, Japanese Patent Publication No. 02-106,915 and Awata et al., Chemistry, Letters, 371 (1985).

- 5 Awata et al. placed carboxylic acids in the cathode cell to react with tetraethylammonium hydroxide as it was formed.

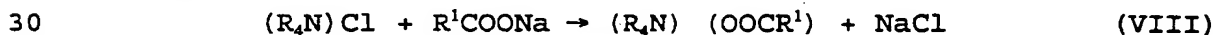
Japanese Patent Publication No. 01-172,363 discloses the preparation of relatively low yields of tetraethylammonium hydroxide by reacting triethylamine with diethyl sulfate,  
10 heating the resultant quat with sulfuric acid to yield the sulfate quat, and reacting the sulfate quat with barium hydroxide to yield the short chain quat, tetraethylammonium hydroxide, and barium sulfate.

- Di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium hydroxides prepared by ion exchange were used as strong bases to digest  
15 animal tissue by Bush et al., French Patent Publication No. 1,518,427.

Akzo discloses that the addition of a metallic hydroxide to a quaternary ammonium chloride such as  
20 didecyldimethylammonium chloride, in an aqueous medium, results in an equilibrium mixture of quaternary ammonium chloride and quaternary ammonium hydroxide (VII). This reaction can be driven to the right by the use of isopropanol as a solvent.



Akzo further discloses that the addition of a soap to a quaternary ammonium chloride yields a quaternary ammonium carboxylate (VIII).



Jordan et al., U.S. Patent No. 3,281,458, disclose the preparation of dioctadecyldimethylammonium humate, ditallowdimethylammonium humate, dipentadecyldimethylammonium

humate, and didodecyldimethylammonium humate by reacting humic acid, lignite, aqueous sodium hydroxide and a chloride quat.

Finally, Nakama et al., J.A.C.O.S., 67:717 (1990) report the interaction between anionic and cationic surfactant and particularly sodium laureate and stearyltrimethylammonium chloride, while Linderborg, U.S. Patent No. 4,585,795, disclose the use of synergistic mixtures of the alkali metal salt of certain biocidal organic acids, quaternary ammonium chlorides, and alkyl-pyridinium chlorides as control agents for short-term protection of timber against sapstain fungi and mildew.

Consequently, efforts have been directed to develop a safe, efficient and expedient method to prepare quaternary ammonium compounds that do not require potentially hazardous metal additives to treat wooden substrates effectively.

It has now been believed useful  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl,  $C_8$ - $C_{20}$  alkyl quaternary ammonium hydroxides can be prepared from specific quaternary chlorides and a metal hydroxide.

It has further been discovered that useful  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl,  $C_8$ - $C_{20}$  alkyl quaternary ammonium carbonates can be prepared, particularly by indirect synthesis from  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl,  $C_8$ - $C_{20}$  alkyl quaternary ammonium chlorides, through  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl,  $C_8$ - $C_{20}$  alkyl quaternary ammonium hydroxide intermediates. It has further been discovered that di  $C_8$ - $C_{12}$  alkyl quaternary ammonium carbonate quats are useful in wood preservative systems as they have improved leaching resistance, particularly without the use of the commonly used metal stabilizers or couplers, arsenic, chromium, copper, and zinc or combinations thereof.

Additionally, di  $C_8$ - $C_{12}$  alkyl quaternary ammonium carboxylates and/or borates can be incorporated into metal-free wood preservative systems.  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl,  $C_8$ - $C_{20}$  alkyl carboxylate quats, and particularly the di  $C_8$ - $C_{12}$  alkyl carboxylate quats above, can be prepared by various

methods from C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium chloride (chloride quat(s)) starting materials, including by indirect synthesis through C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium  
5 hydroxide and C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium carbonate intermediates or by direct synthesis. C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl borate quats, and particularly the di C<sub>8</sub>-C<sub>12</sub> alkyl borate quats above can be prepared by various methods from C<sub>1</sub>-C<sub>20</sub> alkyl or  
10 aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium hydroxide starting materials, which may be prepared as above from the corresponding chloride quats. The di C<sub>8</sub>-C<sub>12</sub> alkyl carbonate and/or borate quats, including those prepared by the methods above, are useful as wood preservatives, as they have  
15 improved leaching resistance, particularly without the use of the commonly used metal stabilizers or couplers, arsenic, chromium, copper, and zinc or combinations thereof.

Typically, quaternary ammonium compounds migrate or leach from wood under wet conditions, however. Common water-  
20 proofing compositions have not proven compatible with the quaternary ammonium compounds typically used in the industry, and therefore, they are not commonly used to hinder the leaching of these quats.

Typical waterproofers are waxes, lower molecular  
25 weight polyolefins, or dispersions or solutions thereof in hydrocarbon solvents. However, quaternary compositions, including those useful in the present invention, typically are water soluble. Generally, they are not soluble in these typical waterproofer solvent systems and are not compatible  
30 with emulsified or dispersed waterproofers.

It has now been discovered that C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl, and particularly di C<sub>8</sub>-C<sub>12</sub> alkyl, quaternary ammonium hydroxides, carbonates, carboxylates, and borates including those prepared by the methods described  
35 herein, are compatible with newly discovered polyhydroxyl or

polyetherhydroxyl esters of fatty acids or polyether hydroxide  
waterproofers. Waterproofing and wood preservative systems  
prepared from the waterproofers or waterproofers and quats de-  
scribed herein exhibit enhanced resistance to leaching and meet  
5 waterproofing standards for heavy duty, ground, or millwork  
applications.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1A is a graphic comparison of leaching of a  
10 wood preservative system according to the present invention and  
a wood preservative system of the prior art.

Figure 1B is an enlarged segment of the graph of  
Figure 1A.

Figure 2A is a graphic comparison of leaching of a  
15 wood preservative system according to the present invention and  
a wood preservative system of the prior art.

Figure 2B is an enlarged segment of the graph of  
Figure 2A.

Figure 3A is a graphic comparison of leaching of  
20 preservative systems according to the present invention and  
wood preservative systems of the prior art.

Figure 3B is an enlarged segment of the graph of  
Figure 3A.

Figure 3C is a graphic comparison of leaching of  
25 preservative systems according to the present invention and  
alternative wood preservative systems.

Figure 4A is a graphic comparison of leaching of  
waterproofer containing wood preservative systems according to  
the present invention and wood preservative systems without  
30 waterproofer.

Figure 4B is an enlarged section of Figure 4A.

#### SUMMARY OF THE INVENTION

A high yield method for the preparation of C<sub>1</sub>-C<sub>20</sub>  
35 alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary

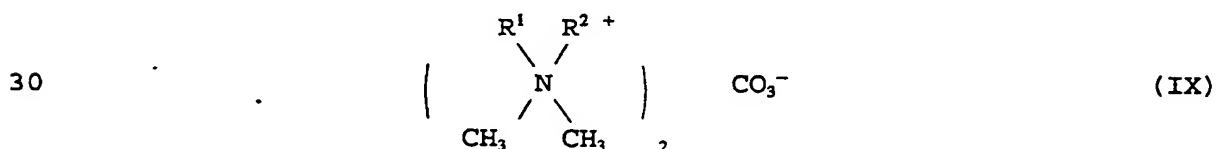
ammonium hydroxide, and preferably di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium hydroxide, which includes the selection of particular solvents, has been discovered. Product yield can be further enhanced by adjustment of the amounts of the reactants. These  
 5 hydroxy quats and wood preservative compositions prepared therefrom can be applied to wood substrates with relatively insignificant leaching from the substrate.

The method of the present invention comprises reacting two reactants, a C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-  
 10 C<sub>20</sub> alkyl quaternary ammonium chloride, preferably a di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium chloride, and a metal hydroxide, in a solvent comprising a C<sub>1</sub>-C<sub>4</sub> normal alcohol. The amount of metal hydroxide reactant is that amount sufficient to yield the C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary  
 15 ammonium hydroxide and a metal chloride. Preferably, this amount is at least a stoichiometric amount.

Also contemplated by the invention are wood preservative systems that preferably are metal-free and which include a biocidal effective amount of at least one di C<sub>8</sub>-C<sub>12</sub>  
 20 alkyl ammonium hydroxide and a solvent. Preferably, the di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium hydroxide is prepared by the method above.

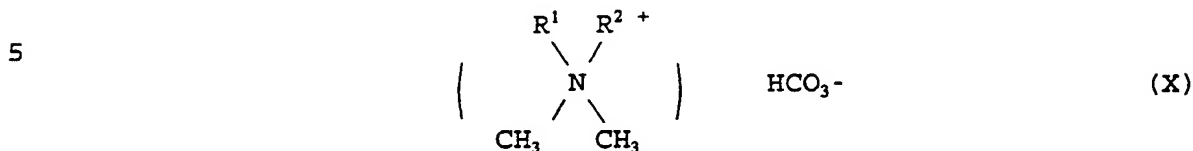
Further contemplated by the invention is a method for preserving a wood substrate. Accordingly, the substrate is  
 25 treated with a these wood preservative systems.

Quaternary ammonium carbonates having the formula

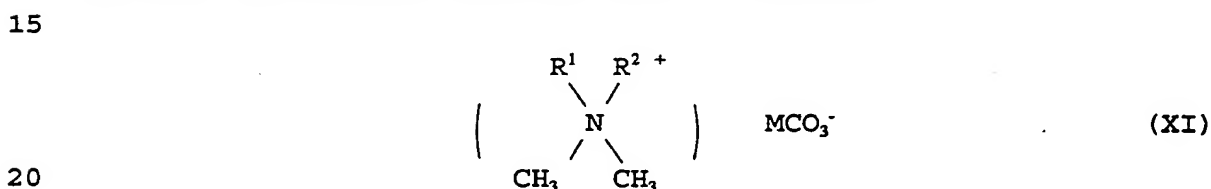


35 wherein R<sup>1</sup> is a C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl group and R<sup>2</sup> is a C<sub>8</sub>-C<sub>20</sub> alkyl group, and preferably wherein R<sup>1</sup> is the same as R<sup>2</sup> and R<sup>1</sup> is a C<sub>8</sub>-C<sub>12</sub> alkyl group, as well as compositions

further comprising the corresponding quaternary ammonium bicarbonate



10 wherein  $R^1$  is the same or a different  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl group as above and  $R^2$  is the same or a different  $C_8$ - $C_{20}$  alkyl group as above, but preferably wherein  $R_1$  is the same as  $R^2$  and  $R^1$  is a  $C_8$ - $C_{12}$  alkyl group; and/or the corresponding quaternary ammonium metal carbonate



wherein  $R^1$  is the same or a different  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl group and  $R^2$  is a  $C_8$ - $C_{20}$  alkyl group; but preferably wherein  $R^1$  is the same as  $R^2$  and  $R^1$  is a  $C_8$ - $C_{12}$  alkyl group and M is a mono-, bi-, or trivalent metal, preferably a monovalent metal, and most preferably an alkali metal, are prepared by reacting two reactants, (a)  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl,  $C_8$ - $C_{20}$  alkyl quaternary ammonium chloride and preferably a di  $C_8$ - $C_{12}$  alkyl quaternary ammonium chloride and

25 (b) a metal hydroxide, in a solvent comprising a  $C_1$ - $C_4$  normal alcohol. The amount of metal hydroxide reactant is that amount sufficient to yield the corresponding  $C_1$ - $C_{20}$  alkyl or aryl-substituted,  $C_8$ - $C_{20}$  alkyl quaternary ammonium hydroxide, and preferably the corresponding di  $C_8$ - $C_{12}$  alkyl quaternary ammonium

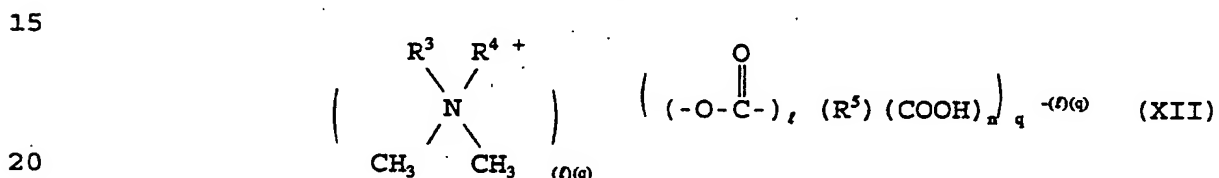
30 hydroxide, a metal chloride, and optionally unreacted metal hydroxide. The resultant quaternary ammonium hydroxide and any unreacted metal hydroxide are then reacted with carbon dioxide to yield the corresponding quaternary ammonium carbonate,

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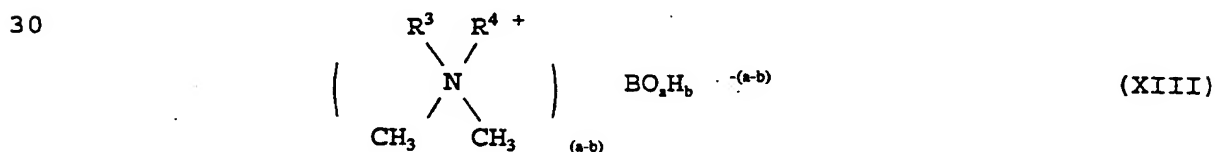
optionally the corresponding quaternary ammonium bicarbonate, and optionally the corresponding quaternary ammonium metal carbonate, or a combination of any of the foregoing, and optionally metal carbonate.

Also contemplated by the invention is a method for preserving a wood substrate. Accordingly, the substrate is treated with a metal coupler-free wood preservative system which comprises (a) a biocidal effective amount of at least one of the above di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium carbonate compounds or compositions, and preferably those prepared by the method above, and (b) a solvent.

Wood preservative systems comprising (a) a biocidal effective amount of (i) at least one di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium carboxylate having the formula



wherein R<sup>3</sup> is a C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl group; R<sup>4</sup> is a C<sub>8</sub>-C<sub>20</sub> alkyl group, but preferably R<sup>3</sup> and R<sup>4</sup> are the same C<sub>8</sub>-C<sub>12</sub> alkyl group; R<sup>5</sup> is a substituted or unsubstituted, interrupted or uninterrupted C<sub>1</sub>-C<sub>100</sub> group; l and q independently are 1, 2 or 3 and (l)(q) is 1, 2, or 3; and n is 0 or an integer from 1 to 50, and (b) a solvent; (ii) at least one di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium borate having the formula



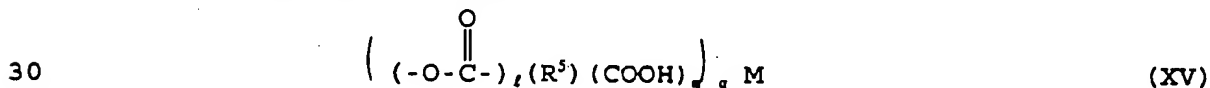
wherein R<sup>3</sup> and R<sup>4</sup> are defined as above, a is 2 or 3, but when a is 2, b is 0 or 1 and when a is 3, b is 0, 1, or 2; or (iii) a combination of (i) and (ii) are also provided.

These carboxylate quats are preferably prepared by indirect or direct synthesis. The indirect synthesis comprises reacting two reactants, a C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl, and preferably a di C<sub>8</sub>-C<sub>12</sub> alkyl, quaternary ammonium chloride and a metal hydroxide, in a solvent comprising a C<sub>1</sub>-C<sub>4</sub> normal alcohol. The amount of metal hydroxide reactant is that amount sufficient to yield a C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium hydroxide (hydroxide quat(s)); and preferably a di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium hydroxide; a metal chloride; and optionally unreacted metal hydroxide. The resultant quaternary ammonium hydroxide and any unreacted metal hydroxide are then reacted with carbon dioxide to yield a C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium carbonate, and preferably a di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium carbonate; and optionally a metal carbonate. The resultant quaternary ammonium carbonate is reacted with carboxylic acid(s) having the formula



wherein R<sup>5</sup>,  $\ell$ , n, and q are defined as above, to yield the carboxylate quat.

Alternatively, the direct synthesis method comprises reacting a C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium chloride, and preferably a di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium chloride, with at least one metal carboxylate having the formula



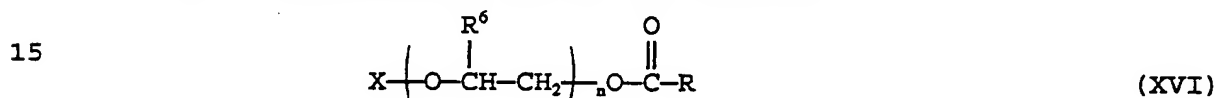
wherein R<sup>5</sup> and n are as defined above; M is a mono-, di-, or tri-valent metal;  $\ell$  and q independently are 1, 2, or 3; and ( $\ell$ )(q) is 1 if M is mono-valent, 2 if M is di-valent, and 3 if M is tri-valent.

These borate quats are preferably prepared by a hydroxy/borate synthesis wherein a hydroxide quat as described above is reacted with boric acid.

Also contemplated by the invention is a method for preserving a wood substrate. Accordingly, the substrate is treated with a wood preservative system which comprises the above di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium carbonate and/or borate wood preservative system, and preferably those that include a carboxylate quat and/or borate quat prepared by the methods above.

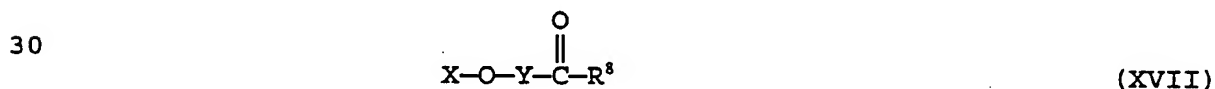
Waterproofer compositions are provided. These waterproofers include

(A) compositions having the formula

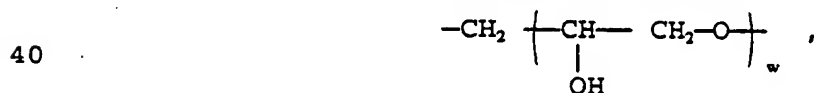


wherein: X is hydrogen or  $\text{R}^7 - \overset{\text{O}}{\parallel} \text{C}$ ;  
 R and R<sup>7</sup> independently are a saturated or unsaturated, substituted or unsubstituted, interrupted or uninterrupted C<sub>9</sub>-C<sub>30</sub> group;  
 R<sup>6</sup> is hydrogen or a methyl group; and  
 n is an integer from 1 to 10.

(B) compositions having the formula:

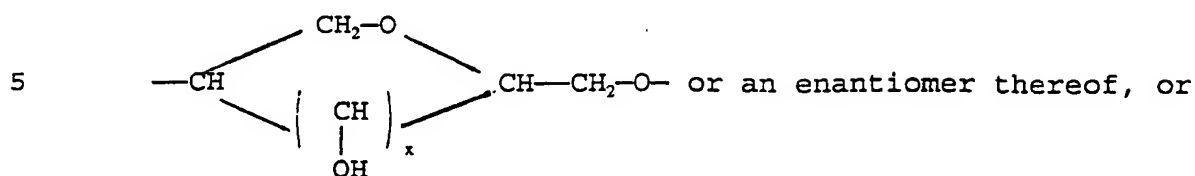


wherein: X is hydrogen or  $\text{R}^9 - \overset{\text{O}}{\parallel} \text{C}$ ;  
 Y is substituted or unsubstituted



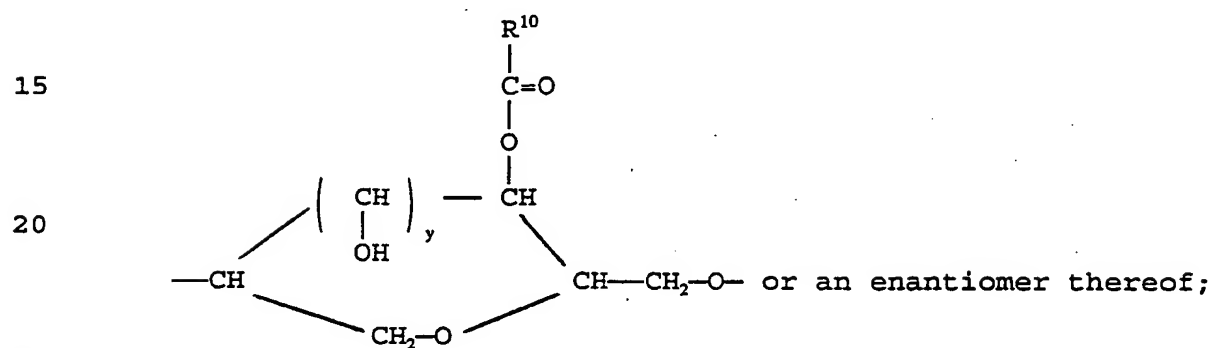
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substituted or unsubstituted



10

substituted or unsubstituted



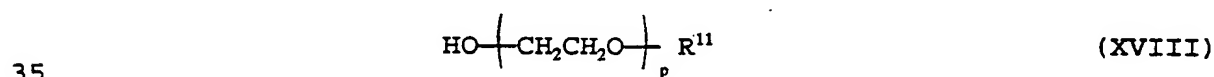
$\text{R}^8$ ,  $\text{R}^9$ , and  $\text{R}^{10}$  independently are a saturated or unsaturated, substituted or unsubstituted, interrupted or uninterrupted  $\text{C}_9\text{-C}_{50}$  group;

$w$  is an integer from 1 to 10; and

$x$  and  $y$  are 0, 1, or 2;

30

(C) compositions having the formula:



wherein:  $\text{R}^{11}$  is a saturated or unsaturated, substituted or unsubstituted, interrupted or uninterrupted  $\text{C}_6\text{-C}_{30}$  group; and

40

$p$  is an integer from 1 to 30; or

(D) any combination of compositions (A), (B), and (C).

Also contemplated by the present invention are the waterproofer systems comprising

(A) a waterproofer enhancing amount of any of the waterproofer compositions (A), (B), (C), or (D) above; and

(B) a solvent.

5 In a preferred embodiment, waterproofer, wood preservative systems comprising

(A) a waterproofing and compatibility enhancing amount of a waterproofer composition as described above;

10

(B) a biocidal effective amount of at least one C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium compositions selected from the group consisting of quaternary ammonium chlorides, hydroxides, carbonates, carboxylates, borates, or any combination thereof; and

15

(C) a solvent, are provided.

Preferred hydroxide quats are di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium hydroxides. Preferred carbonate quats are those having the formula

20

25



wherein R<sup>1</sup> is a C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl group and R<sup>2</sup> is a C<sub>8</sub>-C<sub>12</sub> alkyl group or a mixture of

30

(a) at least one di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium carbonate having the formula

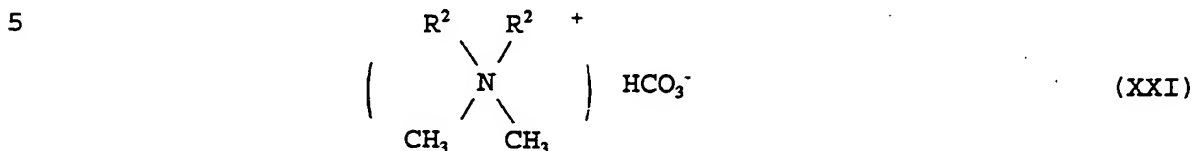
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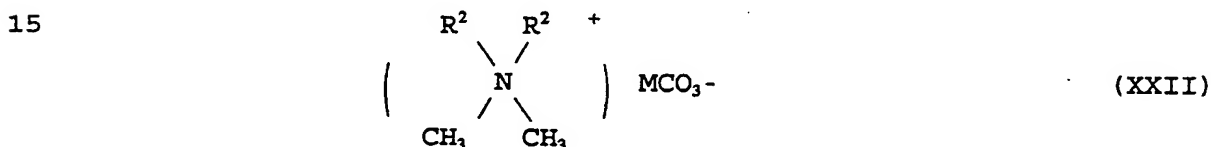
wherein  $R^2$  is a  $C_8-C_{12}$  alkyl group; and

(b) (1) at least one di  $C_8-C_{12}$  alkyl quaternary ammonium bicarbonate having the formula



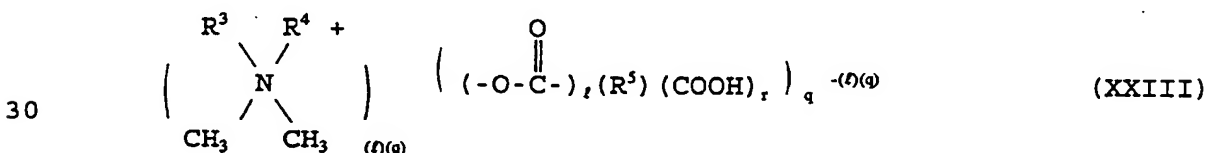
wherein  $R^2$  is the same or a different  $C_8-C_{12}$  alkyl group as in (a); or

(2) at least one di  $C_8-C_{12}$  alkyl quaternary ammonium metal carbonate having the formula

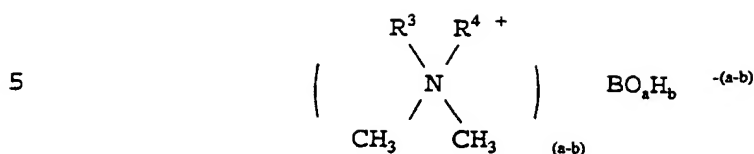


wherein  $R^2$  is the same or a different  $C_8-C_{12}$  alkyl group as in (a) or (b) and M is a non-coupler metal, or

(3) a combination of (b) (1) and (b) (2). Preferred quaternary ammonium carboxylates are those having the formula



wherein  $R^3$  is a  $C_1-C_{20}$  alkyl or aryl-substituted alkyl group;  $R^4$  is a  $C_8-C_{20}$  alkyl group;  $R^5$  is a substituted or unsubstituted, interrupted or uninterrupted,  $C_1-C_{100}$  group;  $\ell$  and  $q$  independently are 1, 2, or 3, and  $(\ell)(q)$  is 1, 2, or 3; and  $r$  is 0 or an integer from 1 to 50. Preferred quaternary ammonium borates are those having the formula

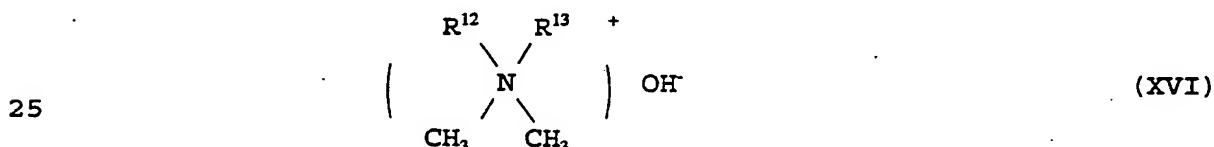


wherein  $R^3$  is a  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl group;  $R^4$  is a  $C_8$ - $C_{20}$  alkyl group,  $a$  is 2 or 3, but when  $a$  is 2,  $b$  is 0 or 1 and when  $a$  is 3,  $b$  is 0, 1 or 2.

In further embodiments, methods for waterproofing or waterproofing and preserving a wood substrate are provided wherein the substrate is treated with the waterproofer or waterproofer preservative systems above.

#### A. Quaternary Ammonium Hydroxide

Although any quaternary ammonium hydroxides are suitable for use in the present invention, quaternary ammonium hydroxides (hydroxy quats) having the formula



wherein  $R^{12}$  is a  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl group,  $R^{13}$  is a  $C_8$ - $C_{20}$  alkyl group, and preferably  $R^{12}$  is the same as  $R^{13}$  and  $R^{12}$  is a  $C_8$ - $C_{12}$  alkyl group, are preferred.

Special mention is made of hydroxy quats wherein  $R^{12}$  is a methyl,  $C_8$  alkyl,  $C_9$  isoalkyl,  $C_{10}$  alkyl,  $C_{12}$  alkyl,  $C_{14}$  alkyl,  $C_{16}$  alkyl, or benzyl group; and  $R^{13}$  is a  $C_{10}$  alkyl,  $C_{12}$ ,  $C_{14}$  alkyl or  $C_{16}$  alkyl group. Most preferred hydroxy quats are didecyldimethylammonium hydroxide wherein  $R^{12}$  and  $R^{13}$  are a  $C_{10}$  alkyl group and most preferably an  $n$ - $C_{10}$  group.

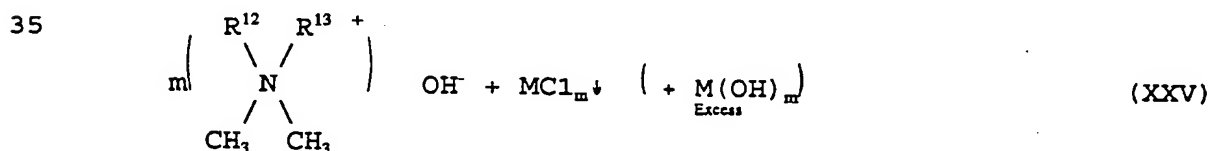
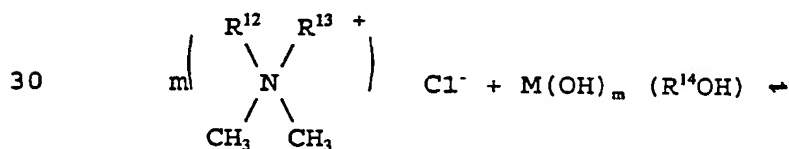
Didecyldimethylammonium hydroxide, when observed in a 70 to 80 percent by weight solution in a 50 percent by weight alcohol/50 percent by weight water solvent, is a yellow/orange liquid. This formulation has a flash point of about 134°F, and

it is a highly alkaline material that reacts with the phenolic OH of lignin.

Quaternary ammonium hydroxides useful in the present invention are preferably prepared according to the reaction  
5 illustrated below.

The method of the present invention provides increased yields of C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium hydroxide, and preferably di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium hydroxide, when compared with  
10 conventional production methods. Although it was previously believed that the reaction of the chloride quat salt with a metal hydroxide to yield quaternary ammonium hydroxide and metal chloride was an equilibrium reaction (VII) or could be driven to the right by the use of branched solvents, it has now  
15 been discovered that by selection of the proper reactants, reaction medium, and/or reaction conditions (including reactant amounts), the reaction can be driven well past equilibrium to yield unprecedented greater amounts of C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium hydroxide.

Although the present method can be used to prepare a variety of C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium hydroxide compounds, the preferred reaction product quat is a di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium hydroxide compound. Most preferred hydroxy quats are di n-C<sub>8</sub>-C<sub>12</sub> alkyl  
25 quaternary ammonium hydroxide, didecyldimethylammonium hydroxide, and di-n-decyldimethylammonium hydroxide.



wherein  $R^{12}$  is a  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl group;  $R^{13}$  is a  $C_8$ - $C_{20}$  alkyl group;  $R^{14}$  is a straight chain  $C_1$ - $C_4$  alkyl group; M is a mono-, di-, or trivalent metal; and m is one if M is monovalent, two if M is divalent, and three if M is trivalent. Preferably  $R^{12}$  is the same as  $R^{13}$ , i.e. a  $C_8$ - $C_{12}$  alkyl group.

Many  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl,  $C_8$ - $C_{20}$  alkyl quaternary ammonium chlorides are suitable reactants, but di  $C_8$ - $C_{12}$  alkyl quaternary ammonium chloride is preferred, and didecyldimethylammonium chloride, and particularly, di-n-decyldimethylammonium chloride is most preferred. The selections of the  $R^{12}$  and  $R^{13}$  substituents of the chloride quat reactant are determinative of the hydroxy quat product.

Special mention is also made of processes wherein  $R^{12}$  is a methyl, butyl,  $C_8$  alkyl,  $C_9$  isoalkyl,  $C_{10}$  alkyl,  $C_{12}$  alkyl,  $C_{14}$  alkyl or benzyl group; and  $R^{13}$  is a  $C_{10}$  alkyl,  $C_{12}$  alkyl,  $C_{14}$  alkyl or  $C_{16}$  alkyl group.

The metal hydroxide reactant is a mono-, bi-, or trivalent metal hydroxide, preferably a monovalent metal hydroxide, and most preferably an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide. Special mention is made of potassium hydroxide. The metal chloride reaction product will precipitate and is easily removed, i.e. by filtration or the like, yielding a hydroxy quat/solvent reaction product. The hydroxy quat can be separated therefrom by drying or the like.

The reaction is conducted in a solvent which comprises a  $C_1$ - $C_4$  normal alcohol. Preferably, the solvent is ethanol, and most preferably, anhydrous ethanol.

The amount of metal hydroxide reactant typically is a stoichiometric amount with respect to the quaternary ammonium chloride reactant. Therefore, on a theoretical basis and if the reaction were complete and unequilibrated, there would be no excess of metal hydroxide reactant upon completion of the

reaction. In practice, yield when using a stoichiometric amount of metal hydroxide reactant will range from about 65% to about 95%, but will vary, dependent in part upon the particular metal hydroxide reactant.

5           Yield can be further improved over conventional methods by utilization of a stoichiometric excess of metal hydroxide ranging from about 2% to about 20% excess. If an excess of metal hydroxide is used, yield will be increased to from about 95% to about 99%, again varying as above.

10           The unreacted metal hydroxide is soluble in the hydroxy quat/solvent mixture. Any excess or unreacted metal hydroxide should be removed after the reaction is completed, and is preferably precipitated by subsequent reaction with carbon dioxide to yield the corresponding metal carbonate. The  
15 carbonate is insoluble in the hydroxy quat/solvent mixture and is easily removed, i.e. by filtration or the like. Alternatively, a solid metal bicarbonate, in which the metal corresponds to the metal of the metal hydroxide, can be added and slurried with the hydroxy quat/solvent mixture. The soluble  
20 metal hydroxide reacts with solid bicarbonate to yield the insoluble metal carbonate. The metal carbonate does not react further with the hydroxy quat.

          Mixing, adding, and reacting of the components in the preparation of these hydroxy quats can be accomplished by  
25 conventional means known to those of ordinary skill in the art. The order of addition of reactants or solvent does not affect the process. Reactants and/or solvent can be added sequentially or simultaneously in any suitable reaction vessel.

          Typically, the reactants and solvent will be stirred  
30 and heated to from about 20°C to about 70°C and held at that temperature for a period of from about 1 hour to about 5 hours. The reaction mixture is then cooled, first to room temperature and then to about 0°C where it is held for about 1 hour to about 2 hours. Any precipitated metal chloride is collected as  
35 is known in the art, i.e. such as by filtration.

Alternatively, the reactants and solvent can be stirred at a slightly elevated temperature, i.e. from about 20°C to about 40°C, to yield the hydroxy quat/solvent mixture. Hydroxy quat can be separated as above.

5 Di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium hydroxides, and particularly those prepared by the method of the present invention, can be formulated as metal-free wood preservative systems. These systems include biocidal effective amounts of at least one hydroxy quat and a suitable solvent, including  
10 aqueous and non-aqueous solvents. Preferably, the solvent is an aqueous solvent including, but not limited to, water, aqueous alcohol such as ethanol, ammonia water, and the like, or a combination of any of the foregoing.

Although other conventional additives may be added as  
15 required for application to different substrates and for different uses as known to those of ordinary skill in the art, metal stabilizers are not required and, in fact, are not recommended to inhibit leaching of the quat from the substrate. Accordingly, wood substrates, such as lumber, timber, or the  
20 like, can be treated with preservative systems which comprise the above hydroxy quat(s) diluted in a suitable solvent as above.

The amount of di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium hydroxide used to treat the substrate is a biocidal effective  
25 amount, i.e. that amount effective to inhibit the growth of or to kill one or more organism that causes wood rot, to inhibit sap staining, or any combination thereof. Such organisms include, but are not limited to, Trametes viride or Trametes versicolor, which cause a white rot; Gaeophyllum trabeum,  
30 which causes a brown rot; and Aspergillus niger, which causes sap stain/mold.

Typically, a wood preservative system will comprise from about 0.1 to about 5 parts by weight of the hydroxy quat and from about 95 to about 99.9 parts by weight of solvent  
35 based upon 100 parts by weight of quat and solvent combined.

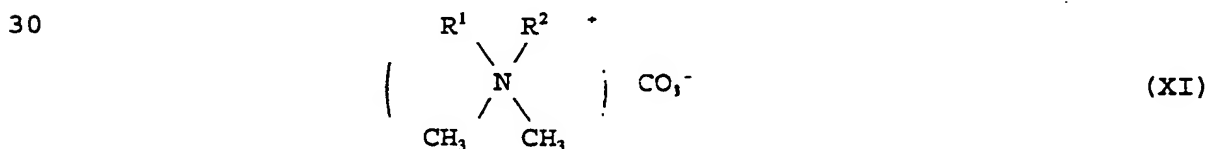
Most preferably, the wood preservative system of the present invention will comprise from about 1 to about 2 parts by weight of hydroxy quat and from about 98 to about 99 parts by weight of solvent on the same basis.

5 Treatment of the substrate is accomplished by any means known to those of ordinary skill in the art including, but not limited to dipping, soaking, brushing, pressure treating or the like. The length of treatment required will vary according to treatment conditions, the selection of which  
10 are known to those skilled in the art.

The wood preservative systems of the present invention display greater resistance to leaching than wood preservatives currently used in the industry. Resistance to leaching is defined as retention of a biocidal effective  
15 amount, and preferably at least about 2% by weight, of hydroxy quat in the substrate over a prolonged period of at least about 100 hours and preferably about 350 hours. Applicants hypothesize, without being bound by any theory, that the hydroxide quat reacts or complexes with the woody matrix of the  
20 substrate, thereby "fixing" it in the substrate. It is also believed that the long chain hydroxy quats and the wood preservative systems that include such quats enhance waterproofing properties of the treated substrates.

25 B. Quaternary Ammonium Carbonate

Although any quaternary ammonium carbonates are suitable for use in the present invention, preferred carbonate quats have the formula



wherein R<sup>1</sup> is a C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl group, R<sup>2</sup> is a C<sub>8</sub>-C<sub>20</sub> alkyl group, and preferably R<sup>1</sup> and R<sup>2</sup> are the same C<sub>8</sub>-C<sub>12</sub> alkyl group.

Special mention is made of carbonate quats wherein R<sup>1</sup> is a methyl, C<sub>8</sub> alkyl, C<sub>9</sub> isoalkyl, C<sub>10</sub> alkyl, C<sub>12</sub> alkyl, C<sub>14</sub> alkyl, C<sub>16</sub> alkyl, or benzyl group; and R<sup>2</sup> is a C<sub>10</sub> alkyl, C<sub>12</sub> alkyl, C<sub>14</sub> alkyl, or C<sub>16</sub> alkyl group.

Most preferred carbonate quats are didecyldimethylammonium carbonate wherein R<sup>1</sup> and R<sup>2</sup> are a C<sub>10</sub> alkyl group and preferably an n-C<sub>10</sub> alkyl group. Didecyldimethylammonium carbonate, when observed as a 70-80 percent by weight solution is a yellow/orange liquid that has a slightly fruity odor. This formulation has a flash point of about 160°F, and it reacts with carboxyl containing compounds.

One or more of these carbonate quats alone or in combination with the corresponding bicarbonate quat(s) and/or metal carbonate salt(s), preferably potassium carbonate salt, can be formulated in the present waterproofer, wood preservative systems.

The stability, and particularly the thermal stability, of carbonate quats is superior to that of hydroxy quats, making these carbonate quats suitable for concentrating and as stock intermediates for further processing.

One or more of these carbonate quats alone or in combination with the corresponding bicarbonate quat(s) and/or metal carbonate salt(s), preferably potassium carbonate salt, can be formulated as metal coupler-free wood preservative systems. These systems include biocidal effective amounts of at least one carbonate quat and a suitable solvent, including aqueous and non-aqueous solvents. Preferably, the solvent is an aqueous solvent including, but not limited to, water, aqueous alcohol such as aqueous ethanol, ammonia water, and the like, or a combination of any of the foregoing.

Although other conventional additives may be added as required for application to different substrates and for

different uses as known to those of ordinary skill in the art, metal stabilizers are not required and, in fact, are not recommended to inhibit leaching of the quat from the substrate. Accordingly, wood substrates, such as lumber, timber, and the like, can be treated with metal coupler-free preservative systems which comprise the above carbonate quat(s) diluted in a suitable solvent as above.

The amount of di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium carbonate(s) used to treat the substrate is a biocidal effective amount, i.e. that amount effective to inhibit the growth of or to kill one or more organism that causes wood rot, to inhibit sap stain, or a combination thereof. Such organisms include, but are not limited to, Trametes viride or Trametes versicolor, which cause a white rot; Goeophyllum trabeum, which causes a brown rot; and Aspergillus niger, which causes sap stain/mold.

Typically, a wood preservative system will comprise from about 0.1 to about 5 parts by weight of the carbonate quat(s) and from about 95 to about 99.9 parts by weight of solvent based upon 100 parts by weight of quat and solvent combined. Most preferably, the wood preservative system of the present invention will comprise from about 1 to about 2 parts by weight of carbonate quat(s) and from about 98 to about 99 parts by weight of solvent on the same basis.

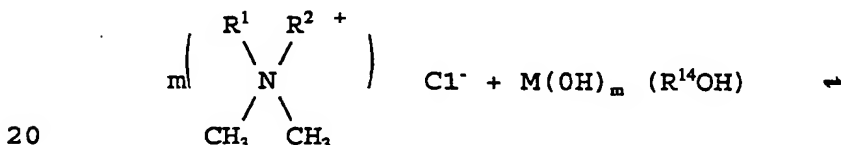
Treatment of the substrate is accomplished by any means known to those of ordinary skill in the art including, but not limited to, dipping, soaking, brushing, pressure treating, or the like. The length of treatment required will vary according to treatment conditions, the selection of which are known to those skilled in the art.

These metal coupler-free preservative systems display greater resistance to leaching than wood preservatives currently used in the industry. Resistance to leaching is defined as retention of a biocidal effective amount, and preferably at least about 2% by weight, of carbonate quat(s) in the substrate over a prolonged period of at least about 100

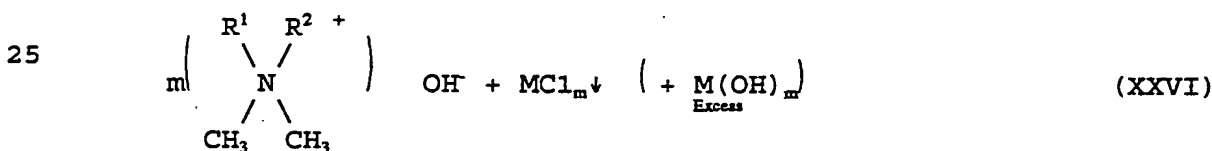
hours and preferably about 350 hours. Applicants hypothesize, without being bound by any theory, that the carbonate quat reacts or complexes with the woody matrix of the substrate, thereby "fixing" it in the substrate. It is also believed that the long chain carbonate quat(s) and the wood preservative systems that include such quats enhance waterproofing properties of treated substrates.

Although certain carbonate quats can be prepared by a variety of methods, applicants have discovered an indirect synthesis method that can be used to prepare a variety of C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium carbonate compounds, preferably di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium carbonate compounds, and most preferably didecyl-dimethylammonium carbonate.

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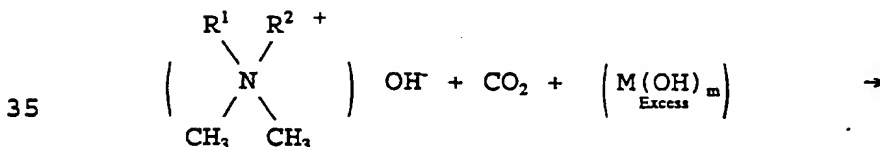


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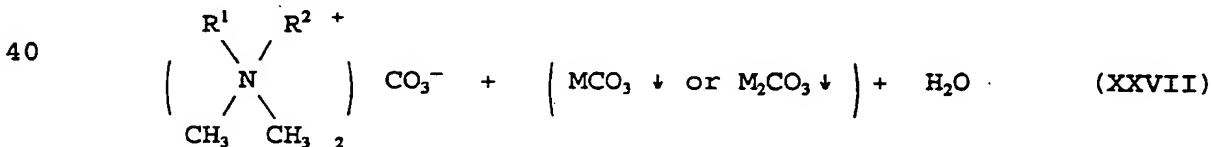


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wherein  $R^1$  is a  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl group;  $R^2$  is a  $C_8$ - $C_{20}$  alkyl group; and preferably  $R^1$  is the same as  $R^2$  and  $R^1$  is a  $C_8$ - $C_{12}$  alkyl group;  $R^{14}$  is a straight chain  $C_1$ - $C_4$  alkyl group; M is a mono-, bi-, tri-valent metal, preferably a mono-valent metal, and most preferably an alkali metal; and m is 1 if M is mono-valent, 2 if M is di-valent, and 3 if M is tri-valent.

A  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl,  $C_8$ - $C_{20}$  alkyl, and preferably a di  $C_8$ - $C_{12}$  alkyl, quaternary ammonium chloride is used as a starting material and is reacted with a metal hydroxide to yield a  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl,  $C_8$ - $C_{20}$  alkyl, and preferably a di  $C_8$ - $C_{12}$  alkyl, quaternary ammonium hydroxide intermediate. The hydroxy quat intermediate(s) and any excess metal hydroxide are then reacted with carbon dioxide to yield the carbonate quat(s) and the metal carbonate.

Many di  $C_8$ - $C_{12}$  alkyl quaternary ammonium chlorides are suitable reactants to prepare the intermediate hydroxy quat and are described above. The selections of the  $R^1$  and  $R^2$  substituents of the chloride quat reactant are determinative of the hydroxy quat intermediate, and therefore, of the carbonate quat product.

The metal hydroxide reactant is also as described above.

The metal chloride first step reaction product will precipitate and is easily removed, i.e. by filtration or the like, yielding a hydroxy quat/solvent reaction product. The hydroxy quat can be separated therefrom by drying or the like, if desired.

The first reaction (XXVI) is conducted in a solvent as described above, and the amount of metal hydroxide reactant is as described above.

Hydroxy quat and any unreacted metal hydroxide are then reacted with at least a stoichiometric equivalent of carbon dioxide to yield the quaternary ammonium carbonate(s), and if any unreacted metal hydroxide is present, the metal

carbonate(s). The conversion of the metal hydroxide to the metal carbonate is the preferred reaction of the two carbonations and will proceed more rapidly. The metal carbonate will precipitate and can be separated easily, i.e. by  
5 filtration or the like, leaving the stable carbonate quat(s) or carbonate quat(s)/solvent reaction product.

The carbonation step can also produce the bicarbonate quat or the metal carbonate quat as byproducts. The carbonate quat alone or in combination with the bicarbonate quat and/or  
10 the metal carbonate quat are suitable for use in the metal coupler-free wood preservative systems of the present invention. These carbonate quats or carbonate/bicarbonate/metal carbonate compositions, do not require a metal coupler for stabilization in a wood substrate. Completely metal-free wood  
15 preservative systems are preferred. However, if a metal carbonate quat is included in the system, preferably the metal is not a metal currently used as a coupler, and most preferably, it is an alkali metal and does not pose environmental or corrosion hazards or concerns.

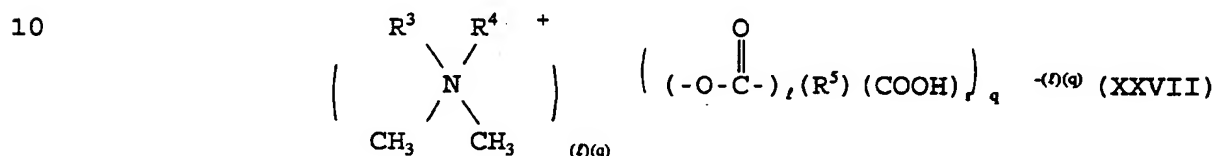
Mixing, adding, and reacting of the components in the preparation of these carbonate quats can be accomplished by conventional means known to those of ordinary skill in the art. The order of addition of reactants or solvent in any individual step does not affect the process. Reactants and/or solvent can  
20 be added sequentially or simultaneously in any suitable reaction vessel. For example, the metal hydroxide may be dissolved in alcohol and the resultant mixture added to the chloride quat or the chloride quat may be dissolved in alcohol and the metal hydroxide added to the resultant mixture.  
25

The carbon dioxide is generally bubbled for a suitable period known to those of ordinary skill in the art through the hydroxy quat/solvent supernatant after the metal chloride precipitate has been separated. Alternatively, the carbon dioxide can be added as solid dry ice directly to the hydroxy  
30 quat. Typically, this time varies from about 0.5 hour to about  
35

1 hour at ambient temperature. Any precipitated metal carbonate is collected as is known in the art, i.e., such as by filtration.

### 5 C. Quaternary Ammonium Carboxylate

Although any quaternary ammonium carboxylates are suitable for use in the present invention, preferred carboxylate quats have the formula



wherein  $R^3$  is a  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl group;  $R^4$  is a  $C_8$ - $C_{20}$  alkyl group; but preferably  $R^3$  and  $R^4$  are the same  $C_8$ - $C_{12}$  alkyl group;  $R^5$  is a substituted or unsubstituted, interrupted or uninterrupted  $C_1$ - $C_{100}$  group;  $l$  and  $q$  independently are 1, 2, or 3, and  $(l)(q)$  is 1, 2, or 3; and  $r$  is 0 or an integer from 1 to 50.

Special mention is also made of carboxylate quats wherein  $R^3$  is a methyl,  $C_8$  alkyl,  $C_9$  isoalkyl,  $C_{10}$  alkyl,  $C_{12}$  alkyl,  $C_{14}$  alkyl or benzyl group; and  $R^4$  is a  $C_{10}$  alkyl,  $C_{12}$  alkyl,  $C_{14}$  alkyl or  $C_{16}$  alkyl group. Most preferred carboxylate quats are didecyldimethylammonium carboxylates wherein  $R^3$  and  $R^4$  are a  $C_{10}$  alkyl group and most preferably an  $n$ - $C_{10}$  alkyl group.

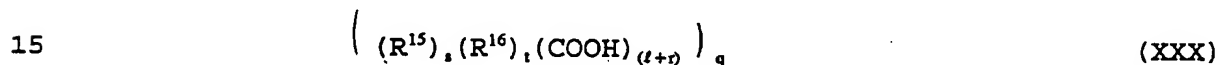
Preferred carboxyl anions are derived from saturated or unsaturated mono- or poly-, including, but not limited to, di- or tri-, carboxylic acids, and particularly  $C_1$ - $C_{20}$  carboxylic acids, or anhydrides thereof.  $R^5$  independently can be substituted, particularly by one or more oxygen or boron atoms or sulfate groups, or interrupted, particularly by one or more oxygen or boron atoms or sulfate groups. Special mention is made of acetic acid, gluconic acid, lauric acid, formic acid, propionic acid, butyric acid, oxalic acid, acrylic acid, tartaric acid, benzoic acid, octanoic acid, and the like.

Additionally, the carboxyl group can be derived from polymeric acids or copolymers in which one or more of the monomers is an acid. An example of a polyacid is polyacrylic acid. Examples of copolymer acids include, but are not limited to, olefin/-  
 5 carboxylic acid polymers such as poly(ethylene/acrylic acid).

Such acids, including the polymeric or copolymeric acids mentioned above are of the formula



10 where  $R^9$ ,  $l$ ,  $r$ , and  $q$  are defined as above. In polymeric copolymers carboxylic acids,  $R^9$  can be represented as  $\left( (R^{11})_l (R^{12})_r \right)$  giving



15 where  $R^{15}$  and  $R^{16}$  independently are substituted or unsubstituted, interrupted or uninterrupted as above  $C_1$ - $C_{100}$  groups and  $s$  and  $t$  independently are integers from 1 to 100. Preferably,  $R^9$ ,  $R^{15}$ ,  
 20 and  $R^{16}$  independently are alkyl or alkenyl groups.

These carboxylate quats can be formulated as metal-free wood preservative systems. These systems include a biocidal effective amount of at least one carboxylate and a suitable solvent including aqueous and non-aqueous solvents.  
 25 Preferably, the solvent is an aqueous solvent including, but not limited to, water, aqueous alcohol, such as ethyl alcohol, ammonia water, aqueous acetic acid, and the like, or a combination of any of the foregoing.

Although other conventional additives may be added to  
 30 these systems as required for application to different substrates and for different uses as known to those of ordinary skill in the art, metal stabilizers are not required and, in fact, are not recommended to inhibit leaching of the quat from the substrate. Accordingly, wood substrates, such as lumber,  
 35 timber, and the like, can be treated with metal-free preserva-

tive systems which comprise the above carboxylate and/or borate quat(s) diluted in a suitable solvent as above.

The amount of quaternary ammonium carboxylate(s) used to treat the substrate is a biocidal effective amount, i.e. that amount effective to inhibit the growth of or to kill one or more organism that causes wood rot, to inhibit sap stain, or a combination thereof. Such organisms include, but are not limited to, Trametes viride or Trametes versicolor, which cause a white rot; Goeophyllum trabeum, which causes a brown rot; and Aspergillus niger, which causes sap stain/mold.

Typically, a wood preservative system will comprise from about 0.1 to about 5 parts by weight of the carboxylate quat(s) and from about 95 to about 99.9 parts by weight of solvent based upon 100 parts by weight of quat(s) and solvent combined. Most preferably, the wood preservative system of the present invention will comprise from about 1 to about 2 parts by weight of carboxylate and from about 98 to about 99 parts by weight of solvent on the same basis.

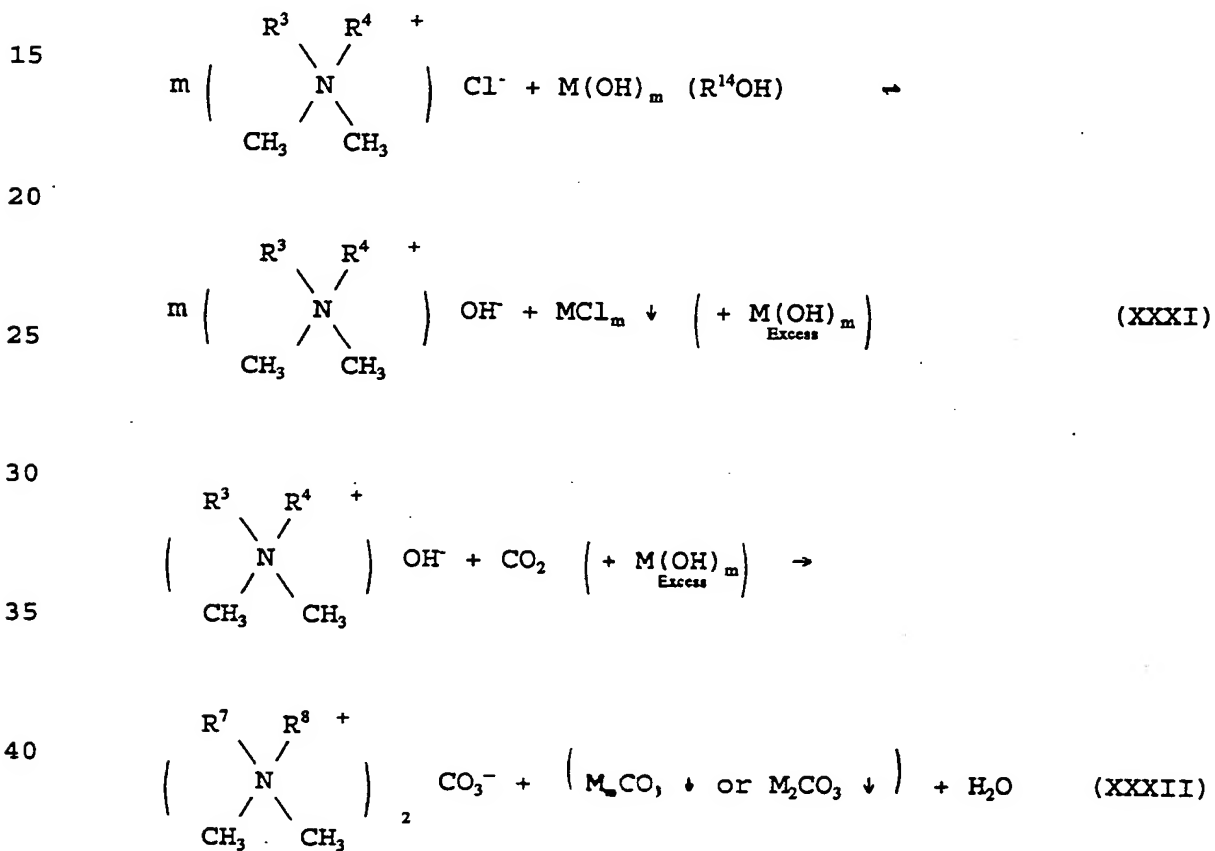
Treatment of the substrate is accomplished by any means known to those of ordinary skill in the art including, but not limited to, dipping, soaking, brushing, pressure treating, or the like. The length of treatment required will vary according to treatment conditions, the selection of which are known to those skilled in the art.

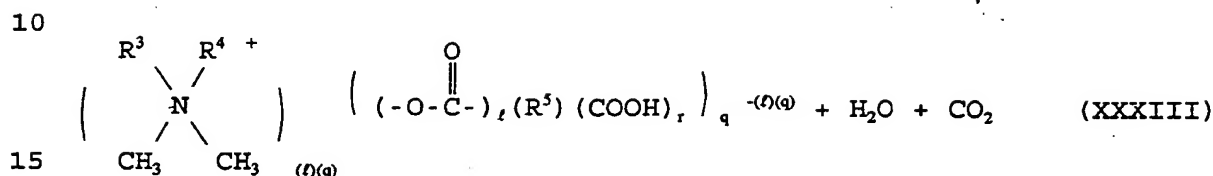
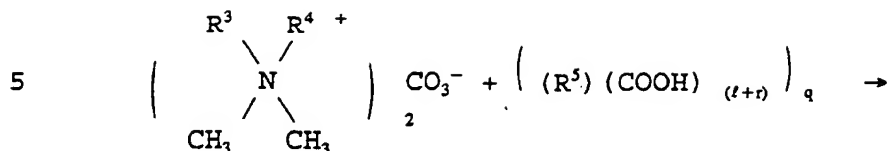
These metal-free wood preservative systems display greater resistance to leaching than wood preservatives currently used in the industry. Resistance to leaching is defined as retention of a biocidal effective amount, and preferably at least about 2% by weight of carboxylate quat(s) in the substrate over a prolonged period of at least about 100 hours and preferably about 350 hours. Applicants hypothesize, without being bound by any theory, that the carboxylate quat(s) may not absorb as quickly to the outside of wood as do conventional wood preservatives, permitting a more complete and uniform treatment of the wood. They may also bond to the wood

directly or through hydrogen bonding to help anchor the quat. Unsaturation in the anion will allow for oxidation and/or polymerization reactions to occur and to fix the quat. It is also believed that the long chain carboxylate quat(s) and the wood preservative systems that include such quats enhance waterproofing properties of treated substrates..

Although the carboxylate quats can be prepared by a variety of methods, preferably they are prepared by an indirect synthesis, a direct synthesis, or a hydroxy quat/acid synthesis.

The indirect synthesis is illustrated below





wherein  $R^3$  is a  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl group;  $R^4$  is a  $C_8$ - $C_{20}$  alkyl group; and preferably  $R^3$  is the same as  $R^4$  and  $R^4$  is a  $C_8$ - $C_{12}$  alkyl group;  $R^5$  is a straight chain  $C_1$ - $C_4$  alkyl group;  $R^9$  is a substituted or unsubstituted, as explained above, interrupted or uninterrupted, as explained above,  $C_1$ - $C_{100}$  group;  $\ell$  and  $q$  independently are 1, 2, or 3 and  $(\ell)(q)$  is 1, 2, or 3;  $M$  is a mono-, bi-, tri-valent metal, preferably a monovalent metal, and most preferably an alkali metal;  $r$  is 0 or an integer from 1 to 50; and  $m$  is 1 if  $M$  is mono-valent, 2 if  $M$  is di-valent, and 3 if  $M$  is tri-valent.

The carboxylate quat is prepared via a carbonate quat intermediate.

A  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl,  $C_8$ - $C_{20}$  alkyl, and preferably a di  $C_8$ - $C_{12}$  alkyl, quaternary ammonium chloride is used as a starting material and is reacted with a metal hydroxide to yield a  $C_1$ - $C_{20}$  alkyl or aryl-substituted alkyl,  $C_8$ - $C_{20}$  alkyl, and preferably a di  $C_8$ - $C_{12}$  alkyl, quaternary ammonium hydroxide intermediate as above. The hydroxy quat intermediate(s) and any excess metal hydroxide are then reacted with carbon dioxide to yield the carbonate quat(s) and the metal carbonate(s) as above. The carbonate quat second intermediate(s) is then reacted with at least one carboxylic acid to yield the carboxylate quat(s). The selection of the  $C_8$ - $C_{12}$  alkyl substituent of the chloride quat reactant is determined.

tive of the hydroxy quat first intermediate, therefore, of the carbonate quat second intermediate, and ultimately, of the cation component of the carboxylate quat product.

The metal hydroxide reactant is described above. The preparation of the hydroxy quat is preferably conducted in a solvent as described above, and the amount of metal hydroxide reactant is described above.

Hydroxy quat and any unreacted metal hydroxide are then reacted with carbon dioxide to yield the quaternary ammonium carbonate(s) as detailed above. The carbonation step can also produce the bicarbonate quat(s) or the metal carbonate quat(s) as by-products.

The carbonate quat second intermediate(s) is then reacted with at least a stoichiometric amount of carboxylic acid(s) to yield the carboxylate quat(s).

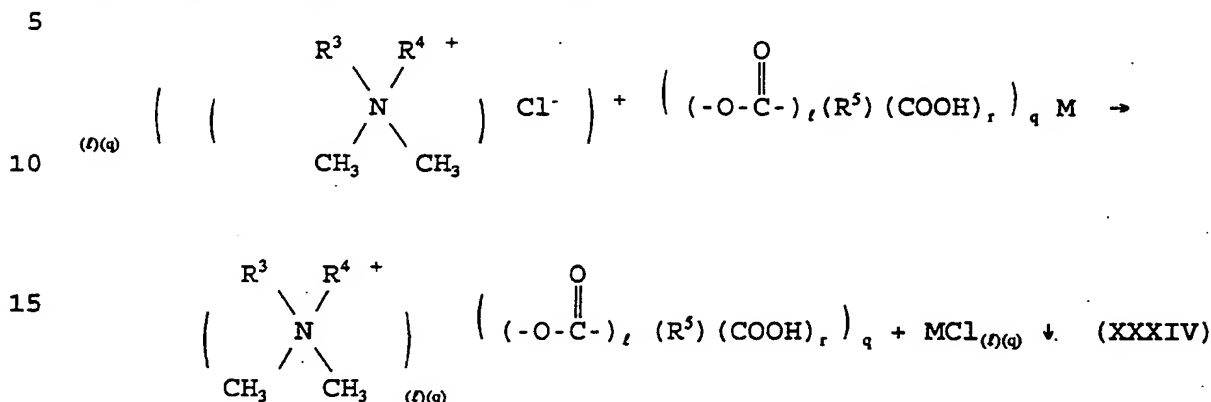
The carboxylic acid(s) in reaction (XXXIII) is typically added over a short period of several minutes, and the reaction typically is rapid. The carboxylate quat(s) can be separated or concentrated by filtration or evaporation after a carbon dioxide evolution in this step is completed.

In the indirect synthesis, any acid having a pKa less than that of carbonic acid, i.e., less than 6.4, such as carboxylic, phosphoric, sulfonic acids, and the like, can be reacted with a carbonate quat and displace carbon dioxide.

The addition of ammonia will retard the carbonate quat and acid reaction (XXXIII). For example, if ammonia is added to a mixture of a polyacid and a carbonate quat, the acid-carbonate quat reaction is retarded. However, when ammonia is slowly evaporated, the reaction liberating carbon dioxide may proceed, yielding a compound that is fixed (insoluble) in wood. Similarly, a system of polyacid and acetic acid should yield an insoluble polyacid quat when the acetic acid evaporates.

Alternatively, the carboxylate quats can be prepared by a direct synthesis method. A metal salt of a carboxylic

acid is reacted with a C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl, and preferably a di-C<sub>8</sub>-C<sub>12</sub> alkyl, quaternary ammonium chloride, in a double replacement reaction, to yield the carboxylate quat and the metal chloride salt



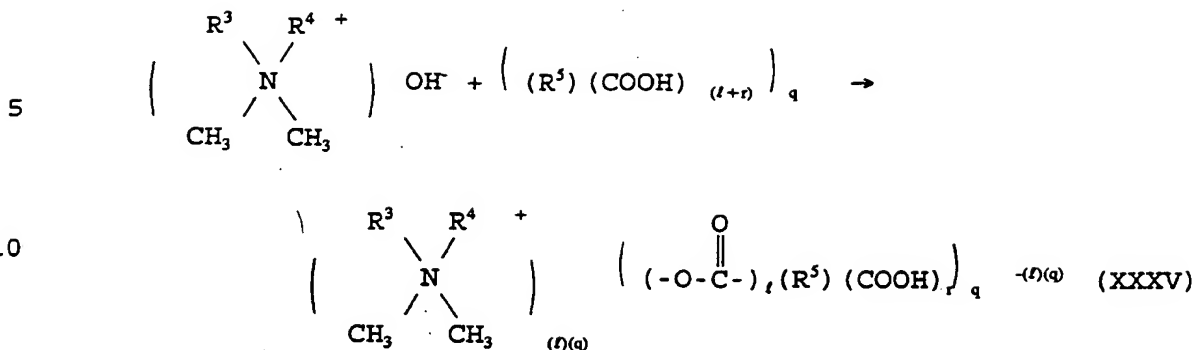
wherein R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, M,  $\ell$ , q, and r are as defined above.

The metal carboxylates are derived from carboxylic acids. The carboxylic acids are as described and detailed above. The metals are mono-, di-, or the tri-valent metals, preferably mono-valent metals and most preferably alkali metals. Special mention is made of potassium and sodium.

Reaction (XXXIV) can be conducted neat or in a number of solvents including, but not limited to ethanol, acetic acid, or propionic acid. Preferably, the solvent comprises a C<sub>1</sub>-C<sub>4</sub> normal alcohol as described above. Yield will depend on the solvent and the reaction conditions selected, which can be determined by one of ordinary skill in the art through routine experimentation in accordance with this detailed explanation.

The chloride quat starting material is selected as above, and again, its selection is determinative of the cation of the carboxylate quat to be formed.

Finally, a third method for the production of the carboxylate quat(s) includes reacting hydroxy quat(s) with carboxylic acid(s).



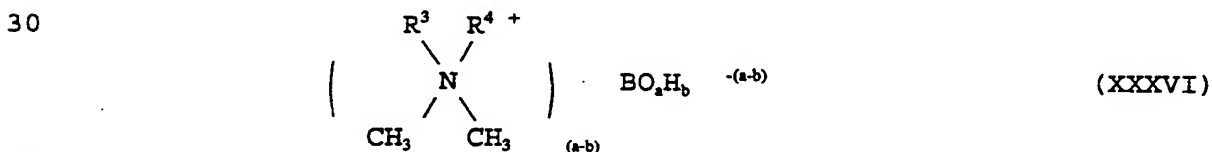
wherein  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ ,  $\ell$ ,  $r$ , and  $q$  are as defined above.

The hydroxy quat(s), carboxylic acid(s), and carboxylate quat(s) are as described above.

Mixing, adding, and reacting of the components in any of the direct, indirect or hydroxy quat/acid methods can be accomplished by conventional means known to those of ordinary skill in the art. The order of addition of reactants or solvent in any individual step does not affect the process.

#### D. Quaternary Ammonium Borate

Although any quaternary ammonium borates are suitable for use in the present invention, preferred borate quats have the formula



wherein  $\text{R}^3$  is a  $\text{C}_1$ - $\text{C}_{20}$  alkyl or aryl-substituted alkyl group;  $\text{R}^4$  is a  $\text{C}_3$ - $\text{C}_{20}$  alkyl group; but preferably  $\text{R}^3$  and  $\text{R}^4$  are the same  $\text{C}_3$ - $\text{C}_{12}$  alkyl group;  $a$  is 2 or 3, but when  $a$  is 2,  $b$  is 0 or 1 and when  $a$  is 3,  $b$  is 0, 1, or 2.

Special mention is also made of borate quats wherein  $\text{R}^3$  is a methyl,  $\text{C}_3$  alkyl,  $\text{C}_9$  isoalkyl,  $\text{C}_{10}$  alkyl,  $\text{C}_{12}$  alkyl,  $\text{C}_{14}$  alkyl or benzyl group; and  $\text{R}^4$  is a  $\text{C}_{10}$  alkyl,  $\text{C}_{12}$  alkyl,  $\text{C}_{14}$  alkyl

or C<sub>16</sub> alkyl group. Most preferred borate quats are didecyl-dimethylammonium borates wherein R<sup>3</sup> and R<sup>4</sup> are a C<sub>10</sub> alkyl group and most preferably an n-C<sub>10</sub> alkyl group.

These borate quats can be formulated as metal-free wood preservative systems. These systems include a biocidal effective amount of at least one carboxylate and a suitable solvent including aqueous and non-aqueous solvents. Preferably, the solvent is an aqueous solvent including, but not limited to, water, aqueous alcohol, such as ethyl alcohol, ammonia water, aqueous acetic acid, and the like, or a combination of any of the foregoing.

Although other conventional additives may be added to these systems as required for application to different substrates and for different uses as known to those of ordinary skill in the art, metal stabilizers are not required and, in fact, are not recommended to inhibit leaching of the quat from the substrate. Accordingly, wood substrates, such as lumber, timber, and the like, can be treated with metal-free preservative systems which comprise the above borate quat(s) diluted in a suitable solvent as above.

The amount of quaternary ammonium borate(s) to treat the substrate is a biocidal effective amount, i.e. that amount effective to inhibit the growth of or to kill one or more organism that causes wood rot, to inhibit sap stain, or a combination thereof. Such organisms include, but are not limited to, Trametes viride or Trametes versicolor, which cause a white rot; Gaeophyllum trabeum, which causes a brown rot; and Aspergillus niger, which causes sap stain/mold.

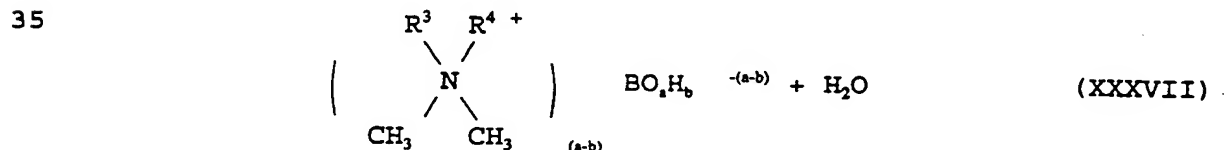
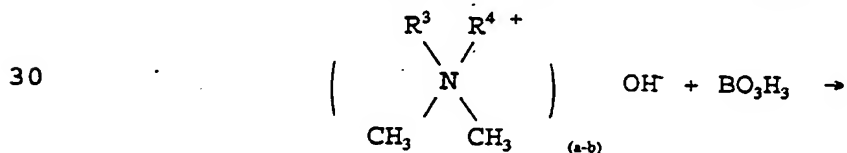
Typically, a wood preservative system will comprise from about 0.1 to about 5 parts by weight of the borate quat(s) and from about 95 to about 99.9 parts by weight of solvent based upon 100 parts by weight of quat(s) and solvent combined. Most preferably, the wood preservative system of the present invention will comprise from about 1 to about 2 parts by weight

of borate quat(s) and from about 98 to about 99 parts by weight of solvent on the same basis.

Treatment of the substrate is accomplished by any means known to those of ordinary skill in the art including, but not limited to, dipping, soaking, brushing, pressure treating, or the like. The length of treatment required will vary according to treatment conditions, the selection of which are known to those skilled in the art.

These metal-free wood preservative systems display greater resistance to leaching than wood preservatives currently used in the industry. Resistance to leaching is defined as retention of a biocidal effective amount, and preferably at least about 2% by weight of borate quat(s) in the substrate over a prolonged period of at least about 100 hours and preferably about 350 hours. Applicants hypothesize, without being bound by any theory, that the borate quat(s) may not absorb as quickly to the outside of wood as do conventional wood preservatives, permitting a more complete and uniform treatment of the wood. They may also bond to the wood directly or through hydrogen bonding to help anchor the quat. Unsaturation in the anion will allow for oxidation and/or polymerization reactions to occur and to fix the quat. It is also believed that the long chain carboxylate quat(s) and the wood preservative systems that include such quats enhance waterproofing properties of treated substrates.

Typically, the production of the borate quat(s) includes reacting hydroxy quat(s) with boric acid.



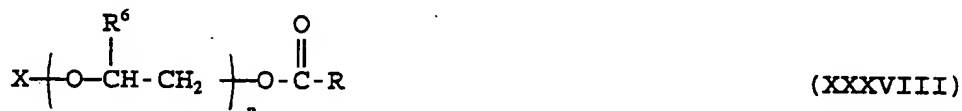
wherein  $R^3$ ,  $R^4$ ,  $R^5$ ,  $a$ , and  $b$  are as defined above.

Mixing, adding, and reacting of the components in the hydroxy quat/acid method can be accomplished by conventional means known to those of ordinary skill in the art. The order of addition of reactants does not affect the process.

#### I. Waterproofers

The polyhydroxyl or polyether hydroxyl fatty acid ester or the polyether hydroxide waterproofers of the present invention are soluble in both aqueous and organic solvent systems. Furthermore, they render the water-soluble quats described herein useful in aqueous or organic systems as well. This occurs despite the fact that these quats alone, i.e. without the present waterproofers, are relatively insoluble in organic solvents, emulsions or dispersions., i.e. they are not generally useful in preserving wood when in an organic solvent.

The waterproofers of the present invention include compositions of the formula:



wherein:  $\text{X}$  is hydrogen or  $\text{R}^7 - \overset{\text{O}}{\parallel} \text{C}$ ;

$\text{R}$  and  $\text{R}^7$  independently are a saturated or unsaturated, substituted or unsubstituted, interrupted or uninterrupted  $\text{C}_9 - \text{C}_{50}$  group;

$\text{R}^6$  is hydrogen or a methyl group; and

$n$  is an integer from 1 to 10.

Saturated  $\text{C}_9 - \text{C}_{50}$  groups include  $\text{C}_9 - \text{C}_{50}$  straight chain, branched, or cycloalkyl groups. Unsaturated  $\text{C}_9 - \text{C}_{50}$  groups include those groups having one or more double or triple bonds or combinations thereof including acyclic groups (including

straight chain or branched), cyclic groups, or combinations thereof. In combinations, unsaturation may occur in the cyclic portion, the acyclic portion, or both. Substituted R or R<sup>2</sup> groups can be substituted with one or more saturated or unsaturated carbon groups with the proviso that the total number of carbon atoms in the R or R<sup>7</sup> group ranges from 9 to 50. These substitutions can give rise to cyclic R or R<sup>7</sup> groups substituted with straight chain or branched, saturated or unsaturated acyclic groups and acyclic R or R<sup>7</sup> groups substituted with saturated or unsaturated cyclic groups. Substituted R or R<sup>7</sup> groups can alternatively or additionally be substituted with one or more oxygen or boron atoms or sulfate groups. Interrupted groups are interrupted by one or more oxygen or boron atoms or sulfate groups.

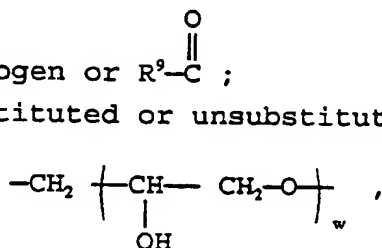
- Special mention is made of
- (A) propylene glycol monostearate, wherein X is hydrogen, R is a C<sub>17</sub> alkyl group, R<sup>6</sup> is a methyl group and n is 1;
  - (B) polyethylene glycol distearate (PEG 400-DS) wherein X is O  

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^7-\text{C} \end{array}$$
R and R<sup>7</sup> each are a C<sub>17</sub> alkyl group, R<sup>6</sup> is hydrogen, and n is 8; and
  - (C) glycol monostearate wherein X is hydrogen, R is a C<sub>17</sub> alkyl group, R<sup>6</sup> is hydrogen, and n is 1.

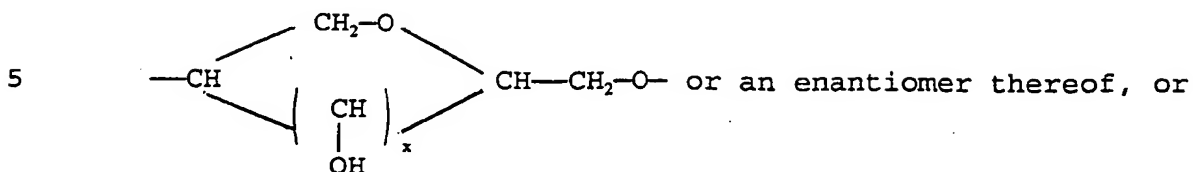
Waterproofers also include compositions of the formula



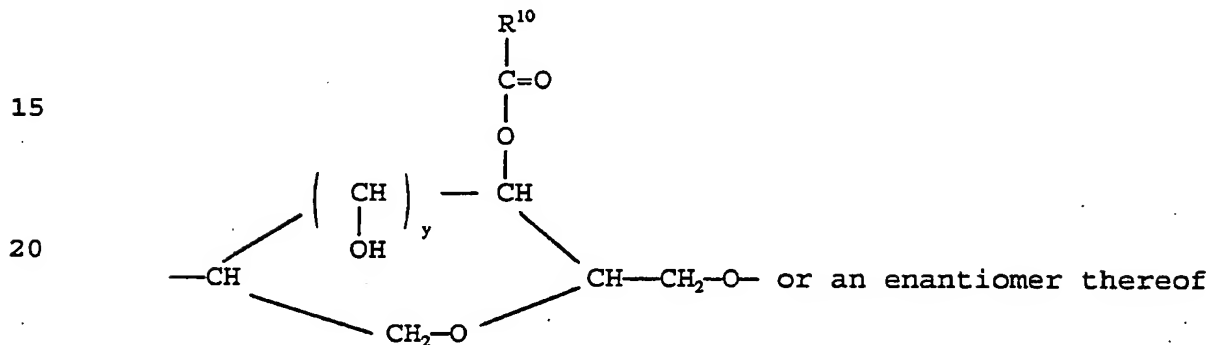
wherein: X is hydrogen or R<sup>9</sup>- $\overset{\text{O}}{\parallel}{\text{C}}$  ;  
 Y is substituted or unsubstituted



substituted or unsubstituted



10 substituted or unsubstituted



25 wherein  $\text{R}^8$ ,  $\text{R}^9$ , and  $\text{R}^{10}$  independently are a saturated or unsaturated, substituted or unsubstituted, interrupted or uninterrupted  $\text{C}_9\text{-C}_{30}$  group; w is an integer from 1 to 10; and x and y are 0, 1, or 2.

30 Y groups can be substituted with one or more  $\text{C}_1\text{-C}_9$  groups with the proviso that the number of carbon atoms in the Y group ranges from 3 to 12, one or more oxygen or boron atoms or sulfate groups or any combination thereof, and can be interrupted by one or more oxygen or boron atoms or sulfate groups.

35 Saturated  $\text{C}_9\text{-C}_{30}$  groups include  $\text{C}_9\text{-C}_{30}$  straight chain, branched, or cycloalkyl groups. Unsaturated  $\text{C}_9\text{-C}_{30}$  groups include those groups having one or more double or triple bonds or combinations thereof including acyclic groups (including straight chain or branched), cyclic groups, or combinations thereof unsaturated groups. In combinations, unsaturation may occur in the cyclic portion, the acyclic portion, or both. Substituted  $\text{R}^3$ ,  $\text{R}^4$ , or  $\text{R}^5$  groups can be substituted with one or more saturated or unsaturated carbon groups with the proviso

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that the total number of carbon atoms in the  $R^8$ ,  $R^9$ , or  $R^{10}$  group ranges from 9 to 50. These substitutions can give rise to cyclic  $R^8$ ,  $R^9$ , or  $R^{10}$  groups substituted with straight chain or branched, saturated or unsaturated groups and acyclic  $R^3$ ,  $R^4$  or  $R^5$  groups substituted with saturated or unsaturated cyclic groups. Substituted  $R^8$ ,  $R^9$ , or  $R^{10}$  groups can alternatively or additionally be substituted with one or more oxygen or boron atoms or sulfate groups. Interrupted groups are interrupted with one or more oxygen or boron atoms or sulfate groups.

Special mention is made of

(A) glycerol monostearate

wherein Y is  $-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{O}-$ , X is hydrogen,  $R^8$

is a  $C_{17}$  alkyl group, and n is 1;

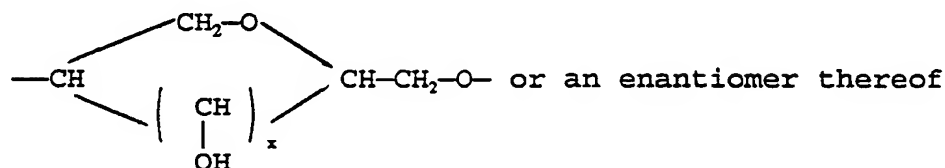
(B) glycerol monolaurate wherein Y is

$-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{O}-$ , X is hydrogen,  $R^8$  is a  $C_{11}$  alkyl

group, and n is 1; and

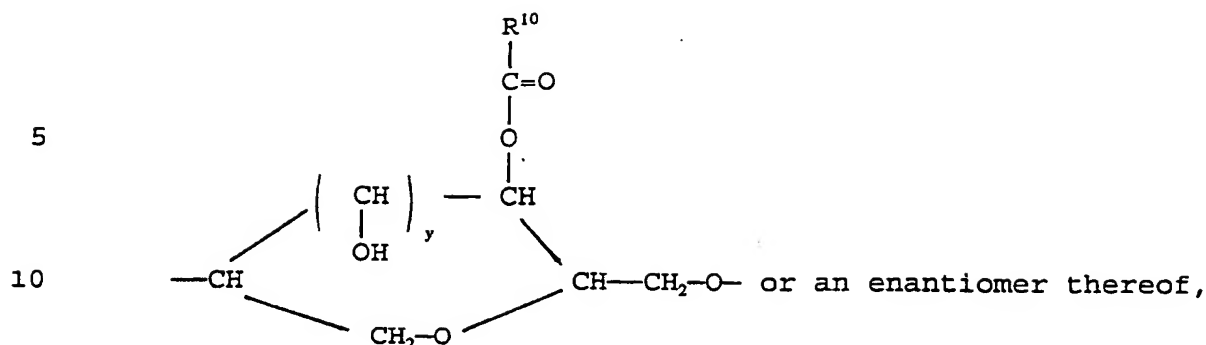
(C) cyclic polyhydroxides such as

(1) sorbitan monostearate wherein Y is



X is hydrogen,  $R^8$  is a  $C_{17}$  alkyl group, and x is 2, or

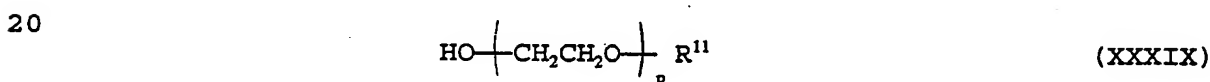
(2) sorbitan tristearate wherein Y is



15

X is  $\text{R}^9 - \text{C}(=\text{O})$ ,  
 $\text{R}^8$ ,  $\text{R}^9$ , and  $\text{R}^{10}$  each are a  $\text{C}_{17}$  alkyl group, and  $y$  is 1.

The waterproofer of the present invention also include compositions of the formula



wherein  $\text{R}^{11}$  is a saturated or unsaturated, substituted or unsubstituted, interrupted or uninterrupted  $\text{C}_6$ - $\text{C}_{30}$  group, and  $p$  is an integer from 1 to 30.

Saturated  $\text{C}_6$ - $\text{C}_{30}$  groups include  $\text{C}_6$ - $\text{C}_{30}$  straight chain, branched, or cycloalkyl groups. Unsaturated  $\text{C}_6$ - $\text{C}_{30}$  groups include those groups having one or more double or triple bonds or combinations thereof including acyclic groups (including straight chain or branched), cyclic groups, or combinations thereof unsaturated groups. In combinations, unsaturation may occur in the cyclic portion, the acyclic portion, or both. Substituted  $\text{R}^{11}$  groups can be substituted with one or more saturated or unsaturated carbon groups with the proviso that the total number of carbon atoms in the  $\text{R}^{11}$  group ranges from 6 to 30. These substitutions can give rise to cyclic  $\text{R}^{11}$  groups substituted with straight chain or branched, saturated or unsaturated acyclic groups and acyclic  $\text{R}^6$  groups substituted with saturated or unsaturated cyclic groups. Substituted  $\text{R}^6$  groups can alternatively or additionally be substituted with

one or more oxygen or boron atoms or sulfate groups. Interrupted groups are interrupted by one or more oxygen or boron atoms or sulfate groups.

Special mention is made of compositions where R<sup>6</sup> is either p-nonylphenyl or C<sub>18</sub> alkyl, and p is 4.

Also contemplated by the present invention are combinations of any of the above waterproofers.

These waterproofers hinder migration of the quat molecules from a substrate under wet conditions. Furthermore, where surface corrosion problems are related to the water holding properties of the quat, the waterproofer displaces or prevents the entry of water.

### III. Solvents

The waterproofer and waterproofer, preservative systems of the present invention include a suitable solvent including aqueous and non-aqueous solvents. Preferably, the solvent is an aqueous solvent including, but not limited to, water, aqueous alcohol, ammonia water, aqueous acetic acid, and the like, or a combination of any of the foregoing. Organic solvents may also be used. These include, but are not limited to, mineral spirits-based solvents and the like.

### IV. Waterproofer Systems and Treatment of Substrates

The amount of waterproofer used in the waterproofer systems of the present invention is a waterproofing enhancing amount, i.e. that amount effective to impart or to increase the water resistance of a substrate treated therewith.

Typically, a waterproofer system will comprise from about 0.1 to about 20 parts by weight of waterproofer and from about 80 to about 99.9 parts by weight of solvent based upon 100 parts by weight of waterproofer and solvent combined. Preferably, the waterproofer system of the present invention will comprise from about 0.2 to about 5 parts by weight of

waterproofers and from about 95 to about 99.8 parts by weight of solvent on the same basis.

The components of the waterproofers systems of the present invention are mixed by conventional means known to those skilled in the art. Other conventional additives may be added as required for application to different substrates and for different uses as known to those of ordinary skill in the art. Wood substrates, such as lumber, timber, or the like, can be treated with these systems. Treatment of the substrate is accomplished by any means known to those of ordinary skill in the art including, but not limited to, dipping, soaking, brushing, pressure treating, or the like. The length of treatment time required will vary according to treatment conditions, the selection of which are known to those skilled in the art.

#### IV. Waterproofers, Wood Preservative Systems and Treatment of Substrates

The amount of waterproofers used in the waterproofers, wood preservative systems of the present invention is a waterproofing and compatibilizing enhancing amount, i.e. that amount effective to impart or to increase the water resistance, leaching resistance, and/or dimensional stability of the waterproofers, wood preservative system and/or the quat and to enhance the compatibility of the quats of the present invention with a solvent.

The amount of quaternary ammonium composition(s) is a biocidal effective amount, i.e. that amount effective to inhibit the growth of or to kill one or more organism that causes wood rot, to inhibit sap stain, or a combination thereof. Such organisms include, but are not limited to, Trametes viride or Trametes versicolor, which cause a white rot; Gaeophyllum trabeum, which causes a brown rot; and Aspergillus niger, which causes sap stain/mold.

Typically, a waterproofers, wood preservative system will comprise from about 0.1 to about 15 parts by weight of

waterproof(er)s, from about 0.1 to about 10 parts by weight of quat(s), and from about 99.8 to about 75 parts by weight of solvent based upon 100 parts by weight of quat, waterproof(er), and solvent combined. Preferably, the waterproof(er), wood  
5 preservative systems of the present invention will comprise from about 0.5 to about 6 parts by weight of quat(s) from about 0.5 to about 8.5 parts by weight of waterproof(er)s, and from about 96 to about 85.5 parts by weight of solvent on the same basis.

10 The components of the waterproof(er), wood preservative systems of the present invention are mixed by conventional means known to those skilled in the art preferably to form an emulsion. Preferably, the waterproof(er) and the quat are melted together. The melt can then be stirred, and warm water (about  
15 40 to 50°C) added with stirring to yield an emulsion or solution. Emulsions prepared in this manner may be stable for periods of at least one year.

Although other conventional additives including, but not limited to, emulsifiers may be added as required for  
20 application to different substrates and for different uses as known to those of ordinary skill in the art, metal stabilizers are not required and, in fact, are not recommended to inhibit leaching of the quat from the substrate. Accordingly, wood substrates, such as lumber, timber, or the like, can be treated  
25 with these systems.

Treatment of the substrate is accomplished by any means known to those of ordinary skill in the art including, but not limited to, dipping, soaking, brushing, pressure treating, or the like. The length of treatment required will  
30 vary according to treatment conditions, the selection of which are known to those skilled in the art.

The waterproof(er), wood preservative systems of the present invention display greater resistance to leaching and greater waterproofing properties, as indicated by swell index,  
35 than wood preservatives currently used in the industry. Resis-

tance to leaching is defined as retention of a biocidal effective amount, and preferably at least about 2% by weight, of quat in the substrate over a prolonged period of at least about 100 hours and preferably about 350 hours. Although any positive swell index indicates some waterproofing ability, a swell index of greater than about 50 indicates notable waterproofing properties.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples illustrate the invention without limitation. All parts and percentages are given by weight unless otherwise indicated.

Quaternary compounds are quantified by two phase titration with sodium laurylsulfate and an indicator. The mixture is buffered to a pH of 10.

$$\left( \frac{\text{Swell of Control} - \text{Swell of Sample}}{\text{Swell of Control}} \right) \times 100$$

#### PREPARATION OF HYDROXY QUATS

##### Example 1 - Stoichiometric Amount of Metal Hydroxide

180 grams (0.4 moles) of 80% didecyldimethylammonium chloride in 20% ethanol water (144 grams of DDAC), 180 ml of absolute denatured ethanol (denatured with methanol/isopropanol), and 26 grams (0.4 mole) of 85% potassium hydroxide pellets (22.1 grams of KOH) were mixed in a flask that was purged with nitrogen and equipped with a heating mantle and a magnetic stirrer. The mixture was stirred and heated at 60-70°C for three hours. The mixture was then allowed to cool to room temperature and finally cooled to 0°C for at least one hour.

Potassium chloride precipitated, and the precipitate was collected on a vacuum filter. The solid was washed with

cold ethanol and subsequently was dried, yielding 30 grams of dry potassium chloride. The quat solution was concentrated in a vacuum to about 75% active bases.

Yield was 180 grams of product containing 138 grams  
5 of didecyldimethylammonium hydroxide.

#### Example 2

The procedure of Example 1 was followed, but the mixture was stirred mechanically at 50°C for one hour.

10 Potassium chloride precipitated, and the precipitate was collected on a vacuum filter. The solid was washed with cold ethanol and subsequently was dried, yielding 30 grams of dry potassium chloride.

Yield was 180 grams of product containing 138 grams  
15 of didecyldimethylammonium hydroxide.

#### Example 3

0.022 mole of 85% potassium hydroxide pellets (1.23 grams of KOH) was added to 0.022 mole of 80%  
20 didecyldimethylammonium chloride in 20% ethanol/water ( 8 grams of DDAC) dissolved in 10 ml of ethanol. The resultant mixture was stirred and heated to 70°C and held at this temperature for one-half hour. The pellets dissolved, and a fine precipitate formed. The mixture was then cooled and chilled to 0°C. The  
25 precipitated solid was collected on a filter and washed with cold ethanol. The filtrate was concentrated to yield a yellow/orange oil with a slight amine odor.

Results are summarized in Table 1.

#### 30 Comparative Example 3A

The procedure of Example 3 was followed substituting isopropanol for the ethanol.

Results are illustrated in Table 1.

Example 4

0.022 mole of 85% potassium hydroxide pellets ( 1.23 grams of KOH) was added to 0.022 mole of 80% didecyldimethyl-ammonium chloride in 20% ethanol/water (8 grams of DDAC) dissolved in 10 ml of propanol. The resultant mixture was stirred and heated to 80°C and held at this temperature for one hour. The pellets dissolved, and a fine precipitate formed. The mixture was then cooled and chilled to 0°C. The precipitated solid was collected on a filter and washed with cold ethanol. The filtrate was concentrated to yield a yellow/orange oil with a slight amine odor.

Results are illustrated in Table 1.

Example 5

The procedure of Example 3 was followed substituting sodium hydroxide for the potassium hydroxide.

Results are illustrated in Table 1.

Comparative Example 5A

The procedure of Comparative Example 3 was followed substituting sodium hydroxide for the potassium hydroxide.

Results are illustrated in Table 1.

Example 6

The procedure of Example 4 was followed substituting sodium hydroxide for the potassium hydroxide.

Results are illustrated in Table 1.

TABLE 1						
Preparation of Didecyldimethylammonium Hydroxide from Stoichiometric Amounts of Reactants						
Example	3	3A	4	5	5A	6
Hydroxide	KOH	KOH	KOH	NaOH	NaOH	NaOH
Solvent	Ethanol	Isopropanol	n-propanol	Ethanol	Isopropyl	n-propanol
Conversion %	96	86	95	81	66	83

Examples 3-6 when compared with Comparative Examples 3A and 5A demonstrate that the use of a normal C<sub>1</sub>-C<sub>4</sub> alcohol as a reaction medium enhances conversion of the chloride quat to the hydroxy quat. Furthermore, a comparison of examples 3 and 4 with Examples 5 and 6 illustrates the increase in conversion by the use of the preferred metal hydroxide, potassium hydroxide.

#### Stoichiometric Excess of Metal Hydroxide

##### Example 7

A nitrogen purged reactor equipped with a heating mantle and a magnetic stir bar was charged with 0.4 mole of 80% didecyldimethylammonium chloride (144 grams of DDAC) in 20% ethanol/water, 180 ml of ethanol, and 0.49 mole of 85% potassium hydroxide (27.5 grams of KOH) pellets. The mixture was heated at 60-70°C for 3 hours, allowed to cool to room temperature, and then cooled to 0°C for about one hour to precipitate potassium chloride. The precipitate was collected on a vacuum filter, and the solid was washed with cold ethanol. Potassium chloride yield was 30.8 grams.

The supernatant solution, which contained the hydroxy quat and 0.09 moles of excess potassium hydroxide, was stirred with 2 grams (0.045 moles) of carbon dioxide gas (from dry ice). The mixture was kept cold for an hour and then was

vacuum filtered to remove 7.2 grams (theoretical 6.2 grams) of potassium carbonate.

Conversion percentage to the hydroxy quat was determined to be 99%.

5

#### Treatment of Wood Substrates

##### Example 8

End grain pine wafers were weighed and then soaked with didecyldimethylammonium hydroxide until a weight gain of 10 30% was observed.

The treated wafers were then placed in water and weighed periodically to determine resistance to leaching.

Results are illustrated in Figures 1A and 1B.

##### 15 Comparative Example 8A

The procedure of Example 8 was followed substituting didecyldimethylammonium chloride for the didecyldimethylammonium hydroxide.

Results are illustrated in Figures 1A and 1B.

20 Figures 1A and 1B illustrate that the hydroxy quat resists leaching for extended periods while the chloride quat leaches to levels of 1% or less in a relatively short period.

##### Example 9

25 A 10" x 0.5" x 0.75" piece of ponderosa pine was equilibrated, weighed, and heated for two hours at 60°C. The wood was treated with a treating solution of 2% didecyldimethylammonium hydroxide in water by heating in the solution at 60°C to 80°C for one hour, cooling and standing 30 overnight, and then being subjected to a second warm to cool cycle. The samples were allowed to dry to constant weight, and the uptake was determined by comparing starting and finishing weights.

The samples were then heated for two hours at 60°C, and the weight of the warm treated samples was compared to the over dried sticks before treatment.

Results are illustrated in Table 2.

5

Comparative Example 9A

The procedure of Example 9 was followed, omitting the didecyldimethylammonium hydroxide from the treating solution.

Results are illustrated in Table 3.

10

Comparative Example 9B

The procedure of Example 9 was followed, substituting didecyldimethylammonium chloride for the didecyldimethylammonium hydroxide.

15

Results are illustrated in Table 2

TABLE 2			
Weight Uptake from Quat Solutions			
Example	9	9A	9B
Solvent	Water	Water	Water
Quat	Hydroxide	-	Chloride
Weight Uptake (%)	2.5	0.4	0.6

20

25 Example 9 when compared with Comparative Examples 9A and 9B, respectively, illustrate the ability of the hydroxy quats prepared according to the present invention to be applied to wood substrates. The hydroxy quat is absorbed better than the chloride quat in water, and is absorbed similarly to the  
30 art accepted chloride quat in ammonia/water. However, the hydroxy quats can be used without metal coupling agents in treating wood substrates.

Example 10

A piece of wood was treated according to the procedure of Example 9. The piece of wood was then soaked in water at room temperature for 24 hours, dried to constant weight, and weighed to determine how much chemical remained. The piece of wood was soaked for 96 additional hours (120 hours total), dried to constant weight, and weighed to determine the leaching of quat from the treated wood. The water was changed several times during this period.

Results are illustrated in Table 3.

Comparative Example 10A

A piece of wood was treated according to the procedure of Comparative Example 9A. The piece of wood was then soaked according to the procedure of Example 10.

Results are illustrated in Table 3.

Comparative Example 10B

A piece of wood was treated according to the procedure of Comparative Example 9B. The piece of wood was then soaked according to the procedure of Example 10.

Results are illustrated in Table 3.

TABLE 3			
Leaching of Quat			
Example	10	10A	10B
Solvent	Water	Water	Water
Quat	Hydroxide		Chloride
Weight Uptake (%)	2.5	0.4	0.6
Retained Quat at 24 Hours (Absolute %/Relative %)	2.3/92	-0.2/-	0.5/83
Retained Quat at 120 Hours (Absolute %/Relative %)	1.8/72	-0.2/-	0.4/67

Example 10, when compared with Comparative Examples 10A and 10B, demonstrates the improved retention properties of hydroxy quats prepared according to the present invention over conventional chloride quats, particularly in the absence of metal stabilizers.

#### Preparation of Carbonate Quats

##### Example 11

180 grams (0.4 moles) of 80% didecyldimethylammonium chloride in 20% ethanol water (144 grams DDAC), 180 ml of absolute denatured ethanol (denatured with methanol/isopropanol), and 32 grams (0.49 mole) of 85% potassium hydroxide pellets (27 grams KOH) were mixed in a flask that was purged with nitrogen and equipped with a heating mantle and a magnetic stirrer. The mixture was stirred and heated at 60-70°C for three hours. The mixture was then allowed to cool to room temperature and finally cooled to 5°C.

Potassium chloride precipitated, and the precipitate was collected on a vacuum filter. The solid was washed with cold ethanol and subsequently was dried, yielding 31 grams (calculated yield 29.6 grams) of dry potassium chloride.

The ethanolic solution of the hydroxy quat containing about 0.09 mole of unreacted KOH, was stirred while 50 grams of carbon dioxide (from sublimed carbon dioxide) were bubbled over one half hour. The resultant mixture was then filtered to remove 7.2 grams of potassium carbonate (6.2 grams calculated), and the filtrate was concentrated to yield an orange/brown liquid with 80-85% carbonate quat in water/ethanol and less than 0.1% chloride quat having a product with 98 to 99% exchanged quat purity.

##### Example 12

180 grams (0.4 moles) of 80% didecyldimethylammonium chloride in 20% ethanol water (144 grams DDAC), 180 ml of absolute denatured ethanol (denatured with methanol/isopropanol),

and 32 grams (0.49 mole) of 85% potassium hydroxide pellets (27 grams KOH) were mixed in a flask that was purged with nitrogen and equipped with a heating mantle and a magnetic stirrer. The mixture was heated to 50°C and stirred for one hour.

5 Potassium chloride precipitated, and the precipitate was collected on a vacuum filter. The solid was washed with cold ethanol and subsequently was dried, yielding 31 grams (calculated yield 29.6 grams) of dry potassium chloride.

10 The ethanolic solution of the hydroxy quat containing about 0.09 mole of unreacted KOH, was stirred while 50 grams of carbon dioxide (from sublimed carbon dioxide) were bubbled over one half hour. The resultant mixture was then filtered, and the filtrate was concentrated to yield an orange/brown liquid. Yield was similar to that of Example 11.

15

#### Treatment of Wood Substrates

##### Example 13

End grain pine wafers were weighed and then soaked with didecyldimethylammonium carbonate until a weight gain of 20 30% was observed.

The treated wafers were then placed in water and weighed periodically to determine resistance to leaching.

Results are illustrated in Figures 1A and 1B.

##### 25 Comparative Example 13A

The procedure of Example 13 was followed substituting didecyldimethylammonium chloride for the didecyldimethylammonium carbonate.

Results are illustrated in Figures 2A and 2B.

30

Figures 2A and 2B illustrate that the carbonate quat resists leaching for extended periods while the chloride quat leaches to levels of 1% or less in a relatively short period.

Examples 14 and 15 and Comparative  
Examples 14A, 14B, 15A and 15B

A 10" x 0.5" x 0.75" piece of ponderosa pine was equilibrated, weighed, and heated for two hours at 60°C. The wood was treated with a treating solution of 2% didecyl-dimethylammonium carbonate in water solvent by heating in the solution at 60°C to 80°C for one hour, cooling and standing overnight, and then being subjected to a second warm to cool cycle. The samples were allowed to dry to constant weight, and the uptake was determined by comparing starting and finishing weights.

The samples were then heated for two hours at 60°C, and the weight of the warm treated samples was compared to the oven dried sticks before treatment.

Additional examples were prepared either omitting the carbonate quat, substituting a chloride quat, or using 1% quat in a 3% aqueous ammonia solvent.

Formulations and results are illustrated in Table 4.

20

TABLE 4						
Weight Uptake from Quat Solutions						
Example	14	14A	14B	15	15A	15B
Solvent	Water	Water	Water	3% Ammonia	3% Ammonia	3% Ammonia
Quat	Carbonate	-	Chloride	Carbonate	-	Chloride
Weight Uptake (%)	1.8	-0.4	0.6	1.6	-0.6	2.0

25

Examples 14 and 15, when compared with Comparative Examples 14A, 14B, 15A, and 15B respectively, illustrate the ability of the carbonate quats of the present invention to be applied to wood substrates. The carbonate quat is absorbed better than the chloride quat in water, and is absorbed similarly to the art accepted chloride quat in ammonia/water. However, the carbonate quats can be used without metal coupling agents in treating wood substrates.

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Examples 16 - 19 and Comparative Examples 16A, 16B, 19A and 19B

A piece of wood was treated according to the procedure of Example 14. The piece of wood was then soaked in water at room temperature for 24 hours, dried to constant weight, and weighed to determine how much chemical remained. The piece of wood was soaked for 96 additional hours (120 hours total), dried to constant weight, and weighed to determine the leaching of quat from the treated wood. The water was changed several times during this period.

10 Additional examples were prepared with different quat concentrations, different anions, and different solvents.

Formulations and results are illustrated in Table 5.

TABLE 5									
Leaching of Quat									
Example	16	16A	16B	17	18	19	19A	19B	
Solvent	Water	Water	Water	Water	Water	3% Ammonia	3% Ammonia	3% Ammonia	
Quat	2% Carbonate		2% Chloride	2.5% Carbonate	5% Carbonate	2% Carbonate		2% Chloride	
Weight Uptake (%)	1.8	0.4	0.6	1.1	1.8	1.6	0.6	2	
Retained Quat at 24 Hours (Absolute %/Relative %)	2/110	-0.2/-	0.5/83	-/100+	-/100	1.7/100	-0.3/-	1.7/85	
Retained Quat at 120 Hours (Absolute %/Relative %)	1.6/80	-0.2/-	0.4/67	-/-	-/-	1.2/75	-0.3/-	1.36/65	

Examples 16-19 and particularly Example 12, when compared with Comparative Examples 16A and 16B, and Example 19, when compared with Comparative Examples 19A and 19B, demonstrate the improved retention properties of carbonate quats over conventional chloride quats, particularly in the absence of metal stabilizers.

#### Indirect Synthesis of Carboxylate Quat

##### Example 20 - Didecyldimethylammonium propionate

180 grams (0.4 mole) of 80% didecyldimethylammonium chloride in 20% ethanol water (144 grams of DDAC), 180 ml of absolute denatured ethanol (denatured with methanol/isopropanol), and 32 grams (0.49 mole) of 85% potassium hydroxide pellets (27 grams of KOH) were mixed in a flask that was purged with nitrogen and equipped with a heating mantle and a magnetic stirrer. The mixture was stirred and heated at 60-70°C for three hours. The mixture was then allowed to cool to room temperature and finally cooled to 5°C.

Potassium chloride precipitated, and the precipitate was collected on a vacuum filter. The solid was washed with cold ethanol and subsequently was dried, yielding 31 grams (calculated yield 29.6 grams) of dry potassium chloride.

The ethanolic solution of the hydroxy quat containing about 0.09 mole of unreacted KOH, was stirred while 50 grams of carbon dioxide (from sublimed carbon dioxide) were bubbled over one half hour. The resultant mixture was then filtered to remove 7.2 grams of potassium carbonate (6.2 grams calculated), and the filtrate was concentrated to yield an orange/brown liquid with 80-85% carbonate quat (0.4 mole of carbonate quat) and less than 0.1% chloride for a product with 98 to 99% exchanged quat purity.

The cold product, after filtration, was placed in a closed flask equipped with a condenser, addition funnel, and a tube connected to a water displacement type gas measuring

device. An equivalent (0.4 mole, 29.6 grams), of propionic acid was added to the carbonate quat over five minutes. Immediate gas evolution was noted, and 5.75 liters of gas were collected over 15 minutes. The solvent was removed on a rotary evaporator after the carbon dioxide evolution ceased, and yielded a yellow/orange liquid.

Quat analysis revealed that the product contained 85% active quat with 0.09% free chloride and 99% exchange.

Example 21 - Didecyldimethylammonium acetate

The procedure of Example 1 is followed, substituting 0.4 mole of acetic acid for the propionic acid.

Example 22 - Didecyldimethylammonium 2-ethylhexanoate

The procedure of Example 20 is followed, substituting 0.4 mole of 2-ethylhexanoic acid for the propionic acid.

The product is cloudy.

Example 23 - Didecyldimethylammonium gluconate

The procedure of Example 20 is followed, substituting 0.4 mole of gluconic acid for the propionic acid.

The product is water soluble.

Example 24 - Didecyldimethylammonium octanoate

The procedure of Example 20 is followed, substituting 0.4 mole of octanoic acid for the propionic acid.

Example 25 - Didecyldimethylammonium mixed coconut fatty acid carboxylate

The procedure of Example 20 is followed, substituting 0.4 mole of mixed coconut fatty acid for the propionic acid.

Example 26 - Didecyldimethylammonium laurate

The procedure of Example 20 is followed, substituting 0.4 mole of lauric acid for the propionic acid.

The product is a waxy solid.

Example 27 - Octyldecyldimethylammonium propionate

The procedure of Example 20 was followed, substituting 0.4 mole of 80% octyldecyldimethylammonium chloride for the didecyldimethylammonium chloride to yield octyldecyldimethylammonium propionate.

Example 28 - Octyldecyldimethylammonium acetate

The procedure of Example 21 was followed, substituting 0.4 mole of 80% octyldecyldimethylammonium chloride for the didecyldimethylammonium chloride to yield octyldecyldimethylammonium acetate.

Example 29 - Isononyldecyldimethylammonium 2-ethylhexanoate

The procedure of Example 22 was followed, substituting 0.4 mole of 80% isononyldecyldimethylammonium chloride for the didecyldimethylammonium chloride to yield isononyldecyldimethylammonium 2-ethyl-hexanoate.

Example 30 - Isononyldecyldimethylammonium gluconate

The procedure of Example 23 was followed, substituting 0.4 mole of 80% isononyldecyldimethylammonium chloride for the didecyldimethylammonium chloride to yield isononyldecyldimethylammonium gluconate.

Example 31 - Benzyldodecyldimethylammonium gluconate

The procedure of Example 23 was followed, substituting 0.4 mole of 80% benzyldodecyldimethylammonium chloride for the didecyldimethylammonium chloride to yield benzyldodecyldimethylammonium gluconate.

Example 32 - Benzyldodecyldimethylammonium octanoate

The procedure of Example 24 was followed, substituting 0.4 mole of 80% benzyldodecyldimethylammonium

chloride for the didecyldimethylammonium chloride to yield benzyldodecyldimethylammonium octanoate.

Example 33 - A mixture of benzyldodecyl-, benzyltetradecyl-, and benzylhexadecyldimethylammonium mixed coconut fatty acid carboxylate

The procedure of Example 25 was followed, substituting 0.4 mole of 80% of a mixture of benzyldodecyl-, benzyltetradecyl-, and benzylhexadecyldimethylammonium mixed fatty acid benzyldodecyldimethylammonium chloride for the didecyldimethylammonium chloride to yield a mixture of benzyldodecyl-, benzyltetradecyl-, and benzylhexadecyldimethylammonium mixed coconut fatty acid carboxylate.

Example 34 - A mixture of benzyldodecyl-, benzyltetradecyl-, and benzylhexadecyldimethylammonium laurate

The procedure of Example 26 was followed, substituting 0.4 mole of 80% of a mixture of benzyldodecyl-, benzyltetradecyl-, and benzylhexadecyldimethylammonium chloride for the didecyldimethylammonium chloride to yield a mixture of benzyldodecyl-, benzyltetradecyl-, and benzylhexadecyldimethylammonium laurate.

#### Direct Synthesis of Carboxylate Quat

Example 35 - Didecyldimethylammonium acetate

180 grams (0.4 mole) of 80% didecyldimethylammonium chloride in 20% ethanol water (144 grams of DDAC), 180 ml of anhydrous ethanol, and a stoichiometric excess, 47 grams (0.48 mole), of anhydrous potassium acetate was mixed in a flask that was purged with nitrogen and equipped with a heating mantle, a magnetic stirrer, and a condenser. The mixture was stirred and heated at 60-70°C for two hours. The insoluble potassium acetate crystals slowly dissolved and a finer solid (KCl) separated. The mixture was then cooled to 0°C and vacuum

filtered. The solid washed with cold ethanol to remove 30.7 grams of potassium chloride (theoretical 29.6 grams). The solution was concentrated, cooled, and filtered to remove 6.5 grams of potassium acetate (theoretical 29.6 grams).

Additional fine crystals of potassium acetate settled out on standing. By assay, the light yellow liquid product was determined to be 80% quat with 100% exchange.

Example 36 - Didecyldimethylammonium gluconate

0.0221 mole of sodium gluconate and 0.0221 mole of 80% didecyldimethylammonium chloride in water were mixed in a flask. The mixture was heated and held until evolution of carbon dioxide gas ceased.

The resultant quat was analyzed, and conversion was determined to be less than 20%.

Example 37 - Didecyldimethylammonium 2-ethylhexanoate

0.0221 mole of sodium 2-ethylhexanoate and 0.0221 mole of 80% didecyldimethylammonium chloride in water were mixed in a flask. The mixture was heated and held until evolution of carbon dioxide gas ceased.

The resultant quat was analyzed, and conversion was determined to be 77%.

Example 38 - Didecyldimethylammonium laurate

0.4 mole of sodium laurate and 0.4 mole of 80% didecyldimethylammonium chloride in water were mixed in a flask. The mixture was heated to 60°C and held for 1 hour.

The resultant quat was analyzed, and conversion was determined to be 90%

Example 39 - Didecyldimethylammonium propionate

0.0221 mole of sodium propionate and 0.0221 mole of 80% didecyldimethylammonium chloride in 8 grams of propionic

acid were mixed in a flask. The mixture was heated to 60°C - 80°C and held for 2 hours.

The resultant quat was analyzed, and conversion was determined to be 90%

Example 40 - Didecyldimethylammonium propionate

0.4 mole of potassium propionate and 0.4 mole of 80% didecyldimethylammonium chloride in solid form were mixed in a flask. The mixture was heated to 60°C - 80°C and held for 2 hours.

The resultant quat was analyzed, and conversion was determined to be 91%

Hydroxy Quat/Acid Synthesis

Example 41 - Didecyldimethylammonium propionate

180 grams (0.4 mole) of 80% didecyldimethylammonium chloride in 20% ethanol water (144 grams of DDAC), 180 ml of absolute denatured ethanol (denatured with methanol/-isopropanol), and 26 grams (0.4 mole) of 85% potassium hydroxide pellets (22 grams of KOH) were mixed in a flask that was purged with nitrogen and equipped with a heating mantle and a magnetic stirrer. The mixture was stirred and heated at 60-70°C for three hours. The mixture was then allowed to cool to room temperature and finally cooled to 0°C for at least one hour.

Potassium chloride precipitated, and the precipitate was collected on a vacuum filter. The solid was washed with cold ethanol and subsequently was dried, yielding 30 grams of dry potassium chloride.

The hydroxy quat/ethanol solution was mixed with a stoichiometric amount of propionic acid to yield a yellow/orange liquid having a flash point of 106°F.

Example 42 - Didecyldimethylammonium borate

The procedure of Example 134 is followed substituting 0.4 mole of boric acid for the propionic acid.

The product is a liquid.

Example 43 - Octyldecyldimethylammonium borate

The procedure of Example 42 was followed, substituting 0.4 mole of 80% octyldecyldimethylammonium chloride for the didecyldimethylammonium chloride to yield octyldecyldimethylammonium borate.

Example 44 - Isononyldecyldimethylammonium borate

The procedure of Example 42 was followed, substituting 0.4 mole of 80% isononyldecyldimethylammonium chloride for the didecyldimethylammonium chloride to yield isononyldecyldimethylammonium borate.

Example 45 - Benzyldodecyldimethylammonium borate

The procedure of Example 42 was followed, substituting 0.4 mole of 80% benzyldodecyldimethylammonium chloride for the didecyldimethylammonium chloride to yield benzyldodecyldimethylammonium borate.

Example 46 - A mixture of benzyldodecyl-, benzyltetradecyl-, and benzylhexadecyldimethylammonium borate

The procedure of Example 42 was followed, substituting 0.4 mole of 80% of a mixture of benzyldodecyl-, benzyltetradecyl-, and benzylhexadecyldimethylammonium chloride for the didecyldimethylammonium chloride to yield a mixture of benzyldodecyl-, benzyltetradecyl-, and benzylhexadecyldimethylammonium borate.

Example 47 - Dihexadecyldimethylammonium borate

The procedure of Example 42 was followed, substituting 0.4 mole of 80% dihexadecyldimethylammonium chloride for

the didecyldimethylammonium chloride to yield dihexadecyldimethylammonium borate.

Example 48 - Dodecyltrimethylammonium borate

The procedure of Example 42 was followed, substituting 0.4 mole of 80% dodecyltrimethylammonium chloride for the didecyldimethylammonium chloride to yield dodecyltrimethylammonium borate.

Treatment of Wood Substrate

Example 49 - Didecyldimethylammonium acetate

End grain pine wafers were weighed and then soaked with didecyldimethylammonium acetate in ethanol/water until a weight gain of 45% was observed.

The treated wafers were then placed in water and weighed periodically to determine resistance to leaching.

Results are illustrated in Figures 3A, 3B, and 3C.

Comparative Example 49A - Didecyldimethylammonium chloride

End grain pine wafers were weighed and then soaked with didecyldimethylammonium chloride in 20% ethanol/water until a weight gain of 35% was observed.

The treated wafers were then placed in water and weighed periodically to determine resistance to leaching.

Results are illustrated in Figures 3A, 3B and 3C.

Example 50 - Didecyldimethylammonium borate

End grain pine wafers were weighed and then soaked with didecyldimethylammonium borate in ethanol/water until a weight gain of 30% was observed.

The treated wafers were then placed in water and weighed periodically to determine resistance to leaching.

Results are illustrated in Figures 3A and 3B.

Example 51 - Didecyldimethylammonium methacrylate

End grain pine wafers were weighed and then soaked with didecyldimethylammonium methacrylate in ethanol/water until a weight gain of 30% was observed.

The treated wafers were then placed in water and weighed periodically to determine resistance to leaching.

Results are illustrated in Figures 1A and 1B.

Example 52 - Didecyldimethylammonium gluconate

End grain pine wafers were weighed and then soaked with didecyldimethylammonium gluconate in ethanol/water until a weight gain of 30% was observed.

The treated wafers were then placed in water and weighed periodically to determine resistance to leaching.

Results are illustrated in Figures 3A and 3B.

Example 53 - Didecyldimethylammonium propionate

End grain pine wafers were weighed and then soaked with didecyldimethylammonium propionate in ethanol/water until a weight gain of 30% was observed.

The treated wafers were then placed in water and weighed periodically to determine resistance to leaching.

Results are illustrated in Figures 3A and 3B.

Example 54 - Didecyldimethylammonium 2-ethylhexanoate

End grain pine wafers were weighed and then soaked with didecyldimethylammonium ethylhexanoate in ethanol/water until a weight gain of 35% was observed.

The treated wafers were then placed in water and weighed periodically to determine resistance to leaching.

Results are illustrated in Figure 3C.

Example 55 - Didecyldimethylammonium laurate

End grain pine wafers were weighed and then soaked with didecyldimethylammonium laurate in ethanol/water until a weight gain of 35% was observed.

The treated wafers were then placed in water and weighed periodically to determine resistance to leaching.

Results are illustrated in Figure 3C.

Example 56 - Didecyldimethylammonium decanoate

End grain pine wafers were weighed and then soaked with didecyldimethylammonium decanoate in ethanol/water until a weight gain of 30% was observed.

The treated wafers were then placed in water and weighed periodically to determine resistance to leaching.

Results are illustrated in Figure 3C.

Example 57 - Didecyldimethylammonium stearate

End grain pine wafers were weighed and then soaked with didecyldimethylammonium stearate in ethanol/water until a weight gain of 40% was observed.

The treated wafers were then placed in water and weighed periodically to determine resistance to leaching.

Results are illustrated in Figure 3C.

Example 58 - Didecyldimethylammonium stearate emulsion

End grain pine wafers were weighed and then soaked with didecyldimethylammonium stearate emulsion in water until a weight gain of 6% was observed.

The treated wafers were then placed in water and weighed periodically to determine resistance to leaching.

Results are illustrated in Figure 3C.

Example 59 - Didecyldimethylammonium octanoate

End grain pine wafers were weighed and then soaked with didecyldimethylammonium octanoate in water until a weight gain of 40% was observed.

The treated wafers were then placed in water and weighed periodically to determine resistance to leaching.

Results are illustrated in Figure 3C.

Figures 3A, 3B, and 3C illustrate that the carboxylate quats of the present invention resist leaching for extended periods of time, and better than the chloride quat.

Biocidal Activity

Example 60 - Didecyldimethylammonium acetate

Cultures of A. niger, G. trabeum, T. veride, and L. lepidus were inoculated with varying amounts of 75% of didecyldimethylammonium acetate in water. The concentrations of carboxylate quat at which no growth was observed and the highest concentration at which growth was not affected were averaged.

Results are illustrated in Table 6.

Comparative Example 60A - Didecyldimethylammonium chloride

The procedure of Example 60 was followed, substituting didecyldimethylammonium chloride for the didecyldimethylammonium acetate.

Results are illustrated in Table 6.

Comparative Example 60B - Didecyldimethylammonium chloride/  
iodopropargyl butylcarbamate

The procedure of Example 60 was followed, substituting a mixture of 4 parts of didecyldimethylammonium chloride and 1 part of iodopropargyl butylcarbamate for the didecyldimethylammonium acetate.

Results are illustrated in Table 6.

Example 61 - Didecyldimethylammonium 2-ethylhexanoate

The procedure of Example 60 was followed, substituting didecyldimethylammonium 2-ethylhexanoate for the didecyldimethyl-ammonium acetate.

Results are illustrated in Table 6.

Example 62 - Didecyldimethylammonium laurate

The procedure of Example 60 was followed, substituting didecyldimethylammonium laurate for the didecyldimethylammonium acetate.

Results are illustrated in Table 6.

Example 63 - Didecyldimethylammonium stearate

The procedure of Example 60 was followed, substituting didecyldimethylammonium stearate for the didecyldimethylammonium acetate.

Results are illustrated in Table 6.

Example 64 - Didecyldimethylammonium chloride (DDAC)/  
polypropylene glycol monostearate (PGMS)/water

3 parts of didecyldimethylammonium chloride and 2.5 parts of PGMS are melted together and stirred while 94.5 parts of warm (40°C) water are added to yield a stable emulsion which is suitable for waterproofing and preserving wood.

Example 65 - DDAC/3% PGMS/Mineral Spirits

The method of Example 64 is followed substituting 3 parts of PGMS for the PGMS and 84 parts of mineral spirits for the water.

Example 66 - DDAC/6% PGMS/Mineral Spirits

The method of Example 65 is followed substituting 6 parts of PGMS for the PGMS and 91 parts of mineral spirits for the mineral spirits.

Example 67 - DDAC/8% PGMS/Mineral Spirits

The method of Example 65 is followed substituting 8 parts of PMGS for the PGMS and 89 parts of mineral spirits for the mineral spirits.

Example 68 - DDAC/12% PGMS/Mineral Spirits

The method of Example 65 is followed substituting 12 parts of PGMS for the PGMS and 85 parts of mineral spirits for the mineral spirits.

Example 69 - DDAC/9% ethylene glycol monostearate (EGMS)/Water

The method of Example 64 is followed substituting 9 parts of EGMS for the PGMS and 88 parts of water for the water.

Example 70 - DDAC/10% ethylene glycol distearate (EGDS)/Water

The method of Example 69 is followed substituting 10 parts of EGDS for the EGMS and 87 parts of water for the water.

Example 71 - DDAC/9% sorbitan tristearate (STS)/Water

The method of Example 64 is followed substituting 9 parts of STS for the PGMS and 88 parts of water for water.

Example 72 - DDAC/9% sorbitan monostearate (SMS)/Water

The method of Example 71 is followed substituting 9 parts of SMS for the STS.

Example 73 - DDAC/9% polyethylene glycol distearate (PEG 400-DS)/Water

The method of Example 71 is followed substituting 9 parts of PEG 400-DS for the SMS.

Example 74 - DDAC/9% PEG 400-DS/Mineral Spirits

The method of Example 73 is followed substituting 88 parts of mineral spirits for the water.

Example 75 - Didecyldimethylammonium hydroxide/PGMS/water

The method of Example 64 is followed substituting 3 parts of didecyldimethylammonium hydroxide for the didecyldimethylammonium chloride.

Example 76 - Didecyldimethylammonium carbonate/2.5% PGMS/water

The method of Example 64 is followed substituting 3 parts of didecyldimethylammonium carbonate for the didecyldimethylammonium chloride.

Example 77 - Didecyldimethylammonium carbonate/2.5%  
glycerol monolaureate (GML)/Water

The method of Example 76 is followed substituting 2.5 parts of GML for the PGMS.

Example 78 - Didecyldimethylammonium carbonate/2.5%  
glycerol monostearate (GMS)/Water

The method of Example 77 is followed substituting 2.5 parts of GMS for the GML.

Example 79 - Didecyldimethylammonium acetate/PGMS/water

The method of Example 64 is followed substituting 3 parts of didecyldimethylammonium acetate D for the didecyldimethylammonium chloride.

Example 80 - Didecyldimethylammonium mixed coconut fatty  
acid carboxylate/PGMS/water

The method of Example 64 is followed substituting 5 parts of didecyldimethylammonium mixed coconut fatty acid carboxylate prepared by the method of Procedure G for the didecyldimethylammonium chloride, 5 parts of PGMS for the PGMS, and 90 parts of water for the water.

Example 81 - Didecyldimethylammonium chloride/PGMS/water

End grain pine wafers are weighed and then soaked with a waterproofer, wood preservative system prepared accord-

ing to the method of Example 1 until the samples are saturated with the treating mixture. The samples are then air dried to constant weight to determine the uptake of the waterproofer, wood preservative system.

The treated wafers are removed, dried to constant weight, and weighed periodically to determine resistance to leaching.

The dried treated wafers are soaked in water for 30 minutes to determine swelling. Swell is measured as the increase in length of the sample compared to an untreated control, and the swell index for each is calculated.

Results are illustrated in Table 7 and Figures 4A and 4B.

Comparative Example 81A - Didecyldimethylammonium chloride

The method of Example 81 is followed substituting didecyldimethylammonium chloride for the waterproofer, wood preservative system.

Results are illustrated in Table 7 and Figures 4A and 4B.

Example 82 - DDAC/3% PGMS/Mineral Spirits

The method of Example 81 is followed substituting a waterproofer, wood preservative system prepared according to the method of Example 65 for the waterproofer, wood preservative system.

Results are illustrated in Table 7.

Example 83 - DDAC/6% PGMS/Mineral Spirits

The method of Example 81 is followed substituting a waterproofer, wood preservative system prepared according to the method of Example 66 for the waterproofer, wood preservative system.

Results are illustrated in Table 7.

Example 84 - DDAC/8% PGMS/Mineral Spirits

The method of Example 81 is followed substituting a waterproofer, wood preservative system prepared according to the method of Example 67 for the waterproofer, wood preservative system.

Results are illustrated in Table 7.

Example 85 - DDAC/12% PGMS/Mineral Spirits

The method of Example 81 is followed substituting a waterproofer, wood preservative system prepared according to the method of Example 68 for the waterproofer, wood preservative system.

Results are illustrated in Table 7.

Example 86 - DDAC/9% EGMS/Water

The method of Example 81 is followed substituting a waterproofer, wood preservative system prepared according to the method of Example 69 for the waterproofer, wood preservative system.

Results are illustrated in Table 7.

Example 87 - DDAC/10% EGDS/Water

The method of Example 81 is followed substituting a waterproofer, wood preservative system prepared according to the method of Example 70 for the waterproofer, wood preservative system.

Results are illustrated in Table 7.

Example 88 - DDAC/9% STS/Water

The method of Example 81 is followed substituting a waterproofer, wood preservative system prepared according to the method of Example 71 for the waterproofer, wood preservative system.

Results are illustrated in Table 7.

Example 89 - DDAC/9% SMS/Water

The method of Example 81 is followed substituting a waterproofer, wood preservative system prepared according to the method of Example 72 for the waterproofer, wood preservative system.

Results are illustrated in Table 7.

Example 90 - DDAC/9% PEG 400-DS/Water

The method of Example 81 is followed substituting a waterproofer, wood preservative system prepared according to the method of Example 73 for the waterproofer, wood preservative system.

Results are illustrated in Table 7.

Example 91 - DDAC/9% PEG 400-DS/Mineral Spirits

The method of Example 81 is followed substituting a waterproofer, wood preservative system prepared according to the method of Example 74 for the waterproofer, wood preservative system.

Results are illustrated in Table 1.

Example 92 - Didecyldimethylammonium hydroxide/PGMS/water

The method of Example 81 is followed substituting a waterproofer, wood preservative system prepared according to the method of Example 75 for the waterproofer, wood preservative system.

Results are illustrated in Table 7 and Figures 4A and 4B.

Comparative Example 92A - Didecyldimethylammonium hydroxide

The method of Comparative Example 81A is followed substituting didecyldimethylammonium hydroxide for the didecyldimethylammonium chloride.

Results are illustrated in Table 7 and Figures 4A and 4B.

Example 93 - Didecyldimethylammonium carbonate/2.5% PGMS/water

The method of Example 81 is followed, substituting a waterproofer, wood preservative system prepared according to the method of Example 76 for the waterproofer, wood preservative system.

Results are illustrated in Table 7 and Figures 4A and 4B.

Comparative Example 93A - Didecyldimethylammonium carbonate

The method of Comparative Example 81A is followed substituting didecyldimethylammonium carbonate for the didecyldimethylammonium chloride to yield a clear solution.

Results are illustrated in Table 7 and Figures 4A and 4B.

Example 94 - Didecyldimethylammonium carbonate/2.5% GML/Water

The method of Example 93 is followed substituting 2.5 parts of GML for the PGMS.

Results are illustrated in Table 7.

Example 96 - Didecyldimethylammonium carbonate/2.5% GMS/Water

The method of Example 81 is followed substituting 2.5 parts of GMS for the PGMS.

Results are illustrated in Table 7.

Example 96 - Didecyldimethylammonium acetate/PGMS/water

The method of Example 81 is followed, substituting a waterproofer, wood preservative system prepared according to the method of Example 16, for the waterproofer, wood preservative system.

Results are illustrated in Table 7 and Figures 4A and 4B.

Comparative Example 96A - Didecyldimethylammonium acetate

The method of Comparative Example 81A is followed substituting didecyldimethylammonium acetate for the didecyldimethylammonium chloride.

Results are illustrated in Figures 4A and 4B.

Example 97 - Didecyldimethylammonium mixed coconut fatty acid carboxylate/PGMS/water

The method of Example 81 is followed substituting a waterproofer, wood preservation system prepared according to the method of Example 80 for the waterproofer, wood preservative system to yield an emulsion.

Results are illustrated in Table 7.

Comparative Example 97A - Didecyldimethylammonium mixed coconut fatty acid carboxylate

The method of Comparative Example 81A is followed substituting 5 parts of didecyldimethylammonium mixed coconut fatty acid carboxylate and 95 parts of water for the waterproofer, wood preservative system.

Results are illustrated in Table 7.

Example 98 - PGMS

The method of Example 81 is followed substituting a solution of 8 parts of PGMS and 92 parts of water for the waterproofer, wood preservative system.

Results are illustrated in Table 7.

Comparative Example 98A - Mineral spirits

The method of Example 81 is followed substituting a commercially available wax based biocide/mineral spirit based solution (Woodtreat MB<sup>®</sup> - KopCoat, Inc.) for the waterproofer, wood preservative system.

Results are illustrated in Table 7.

Table 7 illustrates the enhanced properties of waterproofer, wood preservative systems of the present invention.

## Properties of Waterproofer, Wood Preservative Systems

Table 7

[illegible]

## Properties of Waterproofer, Wood Preservative Systems

Table 1 Cont.

Example	92	92A	93	93A	94	95	96	96A	97	97A	98	98A
<u>Composition</u>												
<u>Quat</u>												
Chloride	-	-	-	-	-	-	-	-	-	-	-	-
Hydroxy	3	100	-	-	-	-	-	-	-	-	-	-
Carbonate	-	-	3	100	3	3	-	-	-	-	-	-
Acetate	-	-	-	-	-	-	3	100	-	-	-	-
Mixed Coconut Fatty Acid Carboxylate	-	-	-	-	-	-	-	-	5	5	-	-
<u>Waterproofer</u>												
PGMS	2.5	-	2.5	-	-	-	2.5	-	5	-	8	-
EGMS	-	-	-	-	-	-	-	-	-	-	-	-
EGDS	-	-	-	-	-	-	-	-	-	-	-	-
STS	-	-	-	-	-	-	-	-	-	-	-	-
SMS	-	-	-	-	-	-	-	-	-	-	-	-
PEG 400-DS	-	-	-	-	-	-	-	-	-	-	-	-
GML	-	-	-	-	2.5	-	-	-	-	-	-	-
GMS	-	-	-	-	-	2.5	-	-	-	-	-	-
Wax-Based in Mineral Spirits	-	-	-	-	-	-	-	-	-	-	-	1-2
<u>Solvent</u>												
Water	94.5	-	94.5	-	94.5	94.5	94.5	-	90	95	92	-
Mineral Spirits	-	-	-	-	-	-	-	-	-	-	-	98-99
<u>Properties</u>												
Swell Index (%)	14	-	71	-	14	57	57	-	50	14	0	43
Total Add On (%)	4.8	35	5.1	37	4.2	5.1	4.5	45	10	2.7	3.4	3.4
Solids or Add On Retained at 24 Hours Leaching, at Room Temperature (%)	-	-	-	-	-	-	-	-	103	103	100+	100+
Solids or Add On Retained at 300 Hours Leaching, at Room Temperature (%)	3.5	0	4.5	0	2.1	3.4	3	0	-	-	-	-

5           All patents, applications, articles, publications,  
and test methods mentioned herein are hereby incorporated by  
reference.

10           Many variations of the present invention will suggest  
themselves to those skilled in the art in light of the above  
detailed description. Such obvious variations are within the  
full intended scope of the appended claims.

WHAT IS CLAIMED IS:

1           1. A method for the preparation of C<sub>1</sub>-C<sub>20</sub> alkyl or  
2 aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium hydrox-  
3 ide, said method comprising

4           (a) reacting a C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted  
5 alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium chloride reactant and a  
6 metal hydroxide reactant in a solvent comprising a C<sub>1</sub>-C<sub>4</sub> normal  
7 alcohol, said metal hydroxide being present in an amount  
8 sufficient to yield said C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl,  
9 C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium hydroxide.

1           2. A method as defined in claim 1 wherein said C<sub>1</sub>-  
2 C<sub>20</sub> alkyl or aryl-substituted alkyl is selected from the group  
3 consisting of a methyl, C<sub>8</sub>-C<sub>16</sub> alkyl and benzyl group, and said  
4 C<sub>8</sub>-C<sub>20</sub> alkyl group is a C<sub>10</sub>-C<sub>16</sub> alkyl.

1           3. A method as defined in claim 1, wherein the  
2 alkyl groups are di C<sub>8</sub>-C<sub>12</sub>.

1           4. A method as defined in claim 1 wherein said  
2 quaternary ammonium compounds are didecyldimethylammonium  
3 compounds.

1           5. A method as defined in any of the proceeding  
2 claims, wherein said metal hydroxide comprises potassium  
3 hydroxide.

1           6. A method as defined in any of the proceeding  
2 claims, wherein said C<sub>1</sub>-C<sub>4</sub> normal alcohol comprises ethanol.

1           7. A method for the preparation of didecyldimethyl-  
2 ammonium hydroxide, said method comprising

3           (a) reacting didecyldimethylammonium chloride and  
4 potassium hydroxide in ethanol, said potassium hydroxide being

5 present in at least a stoichiometric amount with respect to  
6 said didecyldimethylammonium chloride.

1 8. A composition prepared by a method of any of the  
2 proceeding claims.

1 9. A wood preservative system comprising (a) a  
2 biocidal effective amount of at least one di C<sub>8</sub>-C<sub>12</sub> alkyl  
3 quaternary ammonium hydroxide and (b) a solvent, wherein said  
4 wood preservative system is metal-free.

1 10. A wood preservative system as defined in claim  
2 13 wherein said di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium hydroxide is  
3 didecyldimethylammonium hydroxide.

1 11. A wood preservative system as defined in claim  
2 13 wherein said solvent is an aqueous solvent.

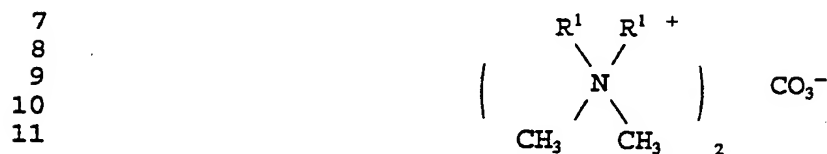
1 12. A wood preservative system as defined in claim  
2 13 comprising from about 0.1 to about 5 parts by weight of di  
3 C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium hydroxide and from about 95 to  
4 99.9 parts by weight of solvent based upon 100 parts by weight  
5 of di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium hydroxide and solvent  
6 combined.

1 13. A wood preservative system as defined in claim  
2 17 wherein said di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium hydroxide is  
3 didecyldimethylammonium hydroxide.

1 14. A wood preservative system comprising a biocidal  
2 effective amount of at least one di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary  
3 ammonium hydroxide prepared by a method as defined in claim 3.

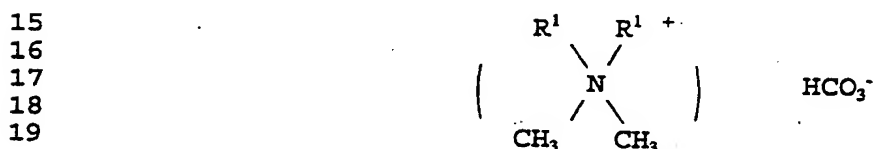
15. A method for preserving a wood substrate comprising treating said wood substrate with a wood preservative system as defined in claim 13.

16. A wood preservative composition comprising  
(a) at least one di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium carbonate having the formula



wherein R<sup>1</sup> is a C<sub>8</sub>-C<sub>12</sub> alkyl group; and

(b) (1) at least one di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium bicarbonate having the formula



wherein R<sup>1</sup> is the same or a different C<sub>8</sub>-C<sub>12</sub> alkyl group as in (a); or

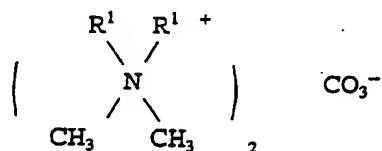
(2) at least one di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium metal carbonate having the formula



wherein R<sup>1</sup> is the same or a different C<sub>8</sub>-C<sub>12</sub> alkyl group as in (a) or (b) and M is a non-coupler metal, or

(3) a combination of (b) (1) and (b) (2);  
said composition being metal coupler-free.

17. A wood preservative system comprising a (A) biocidal effective amount of at least one di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium carbonate having the formulation

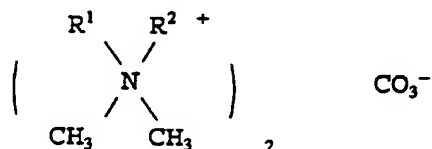


wherein R<sup>1</sup> is a C<sub>8</sub>-C<sub>12</sub> alkyl group and (B) a solvent; wherein said system is metal coupler free.

18. A wood preservative system comprising (A) a biocidal effective amount of at least one composition as defined in claim 1 and (B) a solvent.

19. A wood preservative system as defined in claim 3 comprising from about 0.1 to about 5 parts by weight of di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium carbonate and from about 95 to about 99.9 parts by weight of solvent based upon 100 parts by weight of di C<sub>8</sub>-C<sub>12</sub> alkyl quaternary ammonium carbonate and solvent combined.

20. A method for the preparation of C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium carbonate having the formula



wherein R<sup>1</sup> is a C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl group, and R<sup>2</sup> is a C<sub>8</sub>-C<sub>12</sub> alkyl group, said method comprising

(a) reacting a C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium chloride reactant and a

13 metal hydroxide reactant in a solvent comprising a C<sub>1</sub>-C<sub>4</sub> normal  
 14 alcohol, said metal hydroxide being present in an amount  
 15 sufficient to yield a C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-  
 16 C<sub>20</sub> alkyl quaternary ammonium hydroxide, a metal chloride, and  
 17 optionally unreacted metal hydroxide; and

18 (b) reacting said C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted C<sub>8</sub>-  
 19 C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary  
 20 ammonium hydroxide and optionally any unreacted metal hydroxide  
 21 with carbon dioxide to yield said C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substi-  
 22 tuted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium carbonate and  
 23 optionally a metal carbonate.

1 21. A method as defined in claim 20, wherein R<sup>1</sup> in  
 2 the quaternary ammonium carbonate having the formula compounds



8 is a C<sub>8</sub>-C<sub>12</sub> alkyl group.

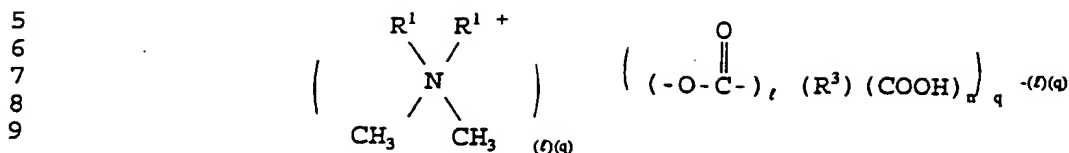
1 22. A method as defined in claim 21 wherein R<sup>1</sup> is a  
 2 C<sub>10</sub> alkyl group.

1 23. A method for preserving a wood substrate com-  
 2 prising treating said wood substrate with a wood preservative  
 3 system as defined in claim 17.

1 24. A composition prepared by a method of any of  
 2 claims 20, 21, 22 or 23.

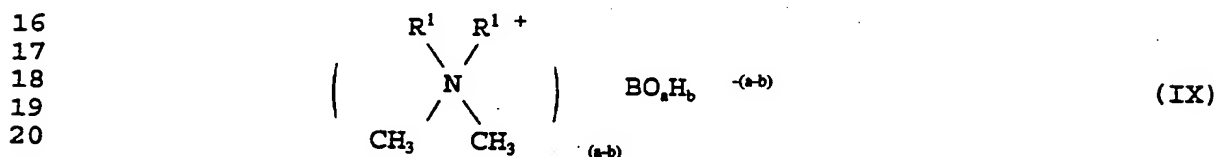
1 25. A wood preservative system comprising  
 2 (a) a biocidal effective amount of  
 3 (i) at least one di-C<sub>8</sub>-C<sub>12</sub> alkyl quaternary  
 4 ammonium carboxylate having the formula

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wherein  $R^1$  is a  $C_8$ - $C_{12}$  alkyl group;  $R^3$  is a substituted or unsubstituted, interrupted or uninterrupted  $C_1$ - $C_{100}$  group;  $\ell$  and  $q$  independently are 1, 2, or 3 and  $(\ell)(q)$  is 1, 2, or 3; and  $n$  is 0 or integer from 1 to 50;

(ii) at least one di- $C_8$ - $C_{12}$  alkyl quaternary ammonium borate having the formula



wherein  $R^1$  is defined as above,  $a$  is 2 or 3, but when  $a$  is 2,  $b$  is 0 or 1, and when  $a$  is 3,  $b$  is 0, 1, or 2; or

(iii) a combination of (i) and (ii); and

(b) a solvent;

said wood preservative system being metal-free.

26. A wood preservative system as defined in claim 25 wherein  $R^1$  is a  $C_{10}$  alkyl group and  $R^3$  is an alkyl or alkenyl group.

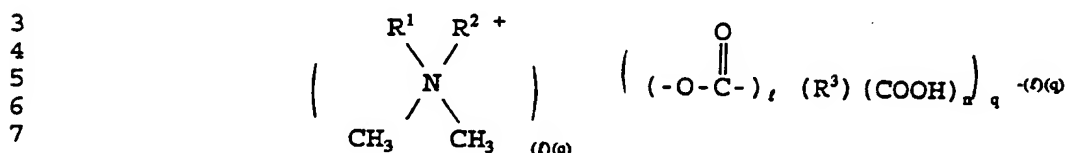
27. A wood preservative system as defined in claim 25 wherein  $\ell$  is 1 or 2.

28. A wood preservative system as defined in claim 25 wherein  $n$  is an integer from 1-20.

29. A wood preservative system as defined in claim 25 comprising from about 0.1 to about 5 parts by weight of di- $C_8$ - $C_{12}$  alkyl quaternary ammonium carboxylate, borate, or

4 combination thereof and from about 95 to about 99.9 parts by  
 5 weight of solvent based upon 100 parts by weight of di-C<sub>8</sub>-C<sub>12</sub>  
 6 alkyl quaternary ammonium carboxylate, borate, or combination  
 7 thereof and solvent combined.

1 30. A method for the preparation of a quaternary  
 2 ammonium carboxylate having the formula

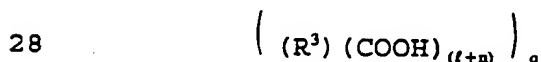


8 wherein R<sup>1</sup> is a C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl group; R<sup>2</sup>  
 9 is a C<sub>8</sub>-C<sub>12</sub> alkyl group; R<sup>3</sup> is a substituted or unsubstituted,  
 10 interrupted or uninterrupted C<sub>1</sub>-C<sub>100</sub> group; *l* and *q* independently  
 11 are 1, 2, or 3 and (*l*)(*q*) is 1, 2, or 3; and *n* is 0 or an  
 12 integer from 1 to 50; said method comprising

13 (a) reacting a C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted  
 14 alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium chloride reactant and a  
 15 metal hydroxide reactant in a solvent comprising a C<sub>1</sub>-C<sub>4</sub> normal  
 16 alcohol, said metal hydroxide being present in an amount  
 17 sufficient to yield a C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-  
 18 C<sub>20</sub> alkyl quaternary ammonium hydroxide, a metal chloride, and  
 19 optionally unreacted metal hydroxide;

20 (b) reacting said C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted  
 21 alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium hydroxide and optionally  
 22 unreacted metal hydroxide with carbon dioxide to yield a C<sub>1</sub>-C<sub>20</sub>  
 23 alkyl or aryl-substituted alkyl, C<sub>1</sub>-C<sub>20</sub> alkyl quaternary ammoni-  
 24 um carbonate and optionally a metal carbonate;

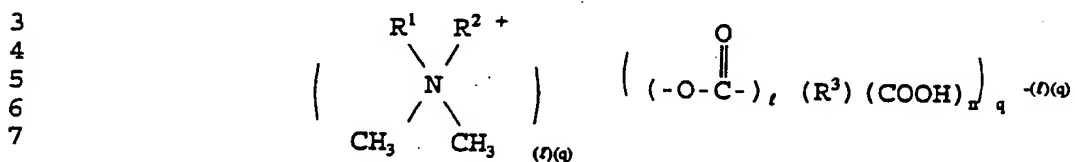
25 (c) reacting said C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted  
 26 alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium carbonate with at least  
 27 one carboxylic acid having the formula



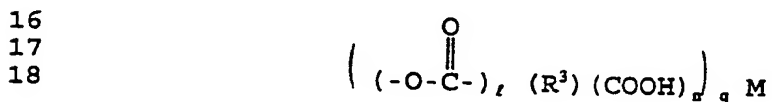
29 wherein R<sup>3</sup> is a substituted or unsubstituted, interrupted or  
 30 uninterrupted C<sub>1</sub>-C<sub>100</sub> group; *l* and *q* independently are 1, 2, or 3  
 31 and (*l*)(*q*) is 1, 2, or 3; and *n* is 0 or an integer from 1 to  
 32 50, to yield said C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub>  
 33 alkyl quaternary ammonium carboxylate.

1 31. A method as defined in claim 30 wherein said di  
 2 C<sub>8</sub>-C<sub>12</sub> alkyl groups are decyl groups.

1 32. A method for the preparation of quaternary  
 2 ammonium carboxylate having the formula



8 wherein R<sup>1</sup> is a C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl group; R<sup>2</sup>  
 9 is a C<sub>8</sub>-C<sub>20</sub> alkyl group; R<sup>3</sup> is a substituted or unsubstituted,  
 10 interrupted or uninterrupted C<sub>1</sub>-C<sub>100</sub> group; *l* and *q* independently  
 11 are 1, 2 or 3 and (*l*)(*q*) is 1, 2, or 3; and *n* is 0 or an  
 12 integer from 1 to 50, said method comprising  
 13 (a) reacting a C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted  
 14 alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium chloride reactant and at  
 15 least one metal carboxylate having the formula



19 wherein R<sup>3</sup> is a substituted or unsubstituted, interrupted or  
 20 uninterrupted C<sub>1</sub>-C<sub>20</sub> groups; M is a mono-, di- or tri-valent  
 21 metal; *l* and *p* independently are 1, 2, 3; (*l*)(*q*) is 1, 2, or 3;  
 22 and *l* is 1 if M is mono-valent, 2 if M is di-valent, or 3 if M  
 23 is tri-valent; and *n* is 0 or an integer from 1 to 50, in a  
 24 solvent comprising a C<sub>1</sub>-C<sub>4</sub> normal alcohol, to yield said quater-  
 25 nary ammonium carboxylate.

1                   33. A method as defined in any of claims 30, 31 or  
2 32, wherein R<sup>1</sup> is a C<sub>8</sub>-C<sub>12</sub> alkyl group.

1                   34. A method for preserving a wood substrate  
2 comprising treating said wood substrate with a wood  
3 preservative system as defined in claim 30.

1                   35. A composition prepared according to a method as  
2 defined in any of claims 30, 31 or 32.

1                   36. A waterproofer composition having the formula  
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3  
4  
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6  
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9  
10  
11  
12  
13  
14  
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16

$$\text{X} - \left( \text{O} - \overset{\text{R}^1}{\underset{|}{\text{CH}}} - \text{CH}_2 \right)_n - \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{R} \quad (\text{I})$$

8 wherein: X is hydrogen or  $\text{R}^2 - \overset{\text{O}}{\parallel} \text{C}$ ;

9 R and R<sup>2</sup> independently are a saturated or unsaturat-  
10 ed, substituted or unsubstituted, interrupted or uninterrupted  
11 C<sub>9</sub>-C<sub>50</sub> group;

12 R<sup>1</sup> is hydrogen or a methyl group; and

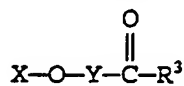
13 n is an integer from 1 to 10; said composition  
14 optionally containing a biocidal effective amount of at least  
15 one C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaterna-  
16 ry ammonium composition, a solvent, or a combination thereof.

1                   37. A waterproofer composition as defined in claim

2  
3  
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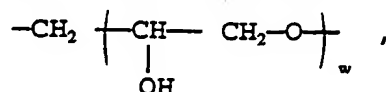
36, wherein X is  $\text{R}^2 - \overset{\text{O}}{\parallel} \text{C}$ , R and R<sup>2</sup> each are a C<sub>17</sub> alkyl group, R<sup>1</sup> is a hydrogen, and n is 1.

38. A waterproofer composition having the formula

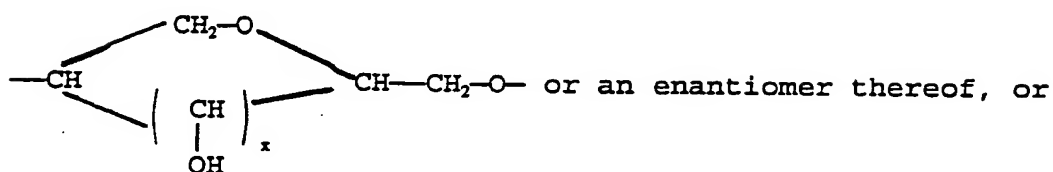


wherein: X is hydrogen or  $\text{R}^4-\overset{\text{O}}{\parallel}\text{C}$ ;

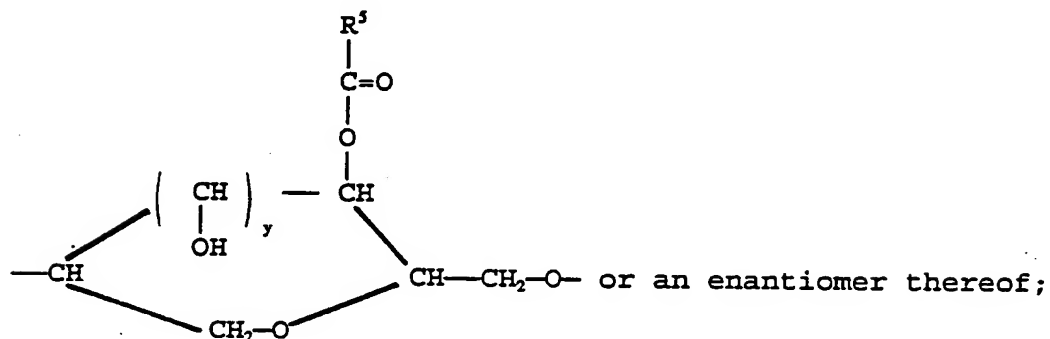
Y is substituted or unsubstituted



substituted or unsubstituted



substituted or unsubstituted



$\text{R}^3$ ,  $\text{R}^4$ , and  $\text{R}^5$  independently are a saturated or unsaturated, substituted or unsubstituted, interrupted or uninterrupted  $\text{C}_9$ - $\text{C}_{30}$  group;

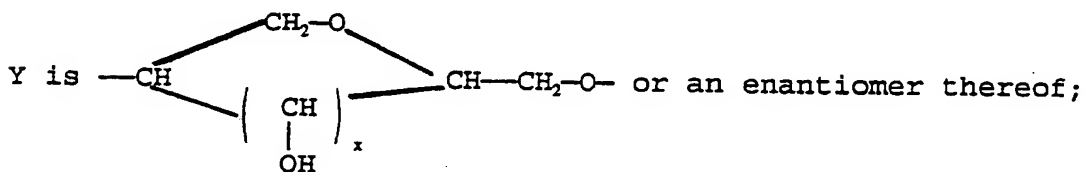
w is an integer from 1 to 10; and

x and y independently are 0, 1, or 2; said composition optionally containing a biocidal effective amount of at least one  $\text{C}_1$ - $\text{C}_{20}$  alkyl or aryl-substituted alkyl,  $\text{C}_8$ - $\text{C}_{20}$  alkyl quaternary ammonium composition, a solvent, or a combination thereof.

1 39. A waterproofer composition as defined in claim  
2 38 wherein: X is hydrogen; R<sup>3</sup> is a C<sub>11</sub> to C<sub>17</sub> alkyl group; and n  
3 is 1.

1 40. A waterproofer composition as defined in claim  
2 38 wherein: X is hydrogen; R<sup>3</sup> is a C<sub>11</sub> alkyl group; and n is 1.

1 41. A water composition as defined in claim 38  
2 wherein: X is hydrogen;

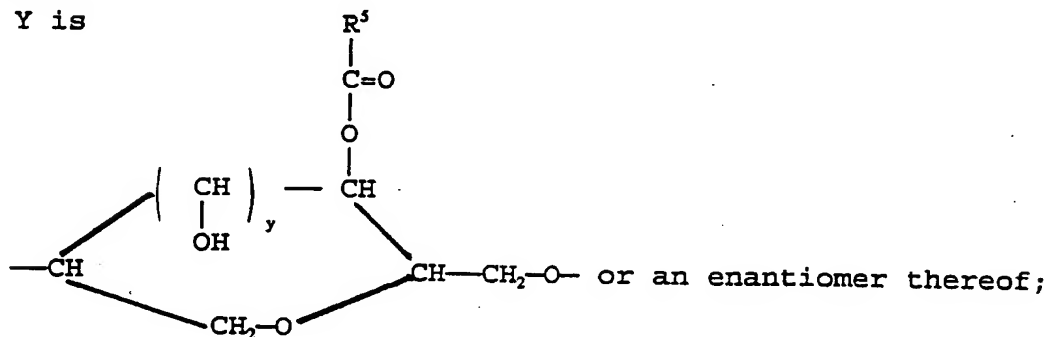


8 R<sup>3</sup> is a C<sub>17</sub> alkyl group; and  
9 x is 2.

1 42. A waterproofer composition as defined in claim 4  
2  
3

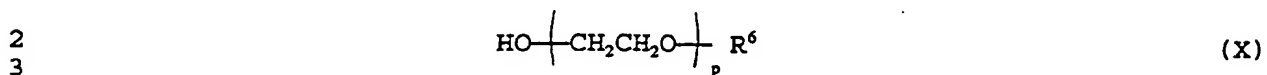
4 wherein: X is R<sup>4</sup>-C(=O);

5 Y is



16 R<sup>3</sup>, R<sup>4</sup>, and R<sup>5</sup> each are a C<sub>17</sub> alkyl group; and  
17 y is 1; said composition optionally containing a  
18 biocidal effective amount of at least one C<sub>1</sub>-C<sub>20</sub> alkyl or aryl-  
19 substituted alkyl, C<sub>8</sub>-C<sub>20</sub> alkyl quaternary ammonium composition,  
20 a solvent, or a combination thereof.

1                    43. A waterproofer composition having the formula



4 wherein:  $R^6$  is a saturated or unsaturated, substituted or  
5 unsubstituted, interrupted or uninterrupted  $C_6$ - $C_{30}$  group; and p  
6 is an integer from 1 to 30; said composition optionally  
7 containing a biocidal effective amount of at least one  $C_1$ - $C_{20}$   
8 alkyl or aryl-substituted alkyl,  $C_8$ - $C_{20}$  alkyl quaternary ammoni-  
9 um composition, a solvent, or a combination thereof.

1 44. A waterproofer composition as defined in claim  
2 43, wherein R<sup>1</sup> is a C<sub>18</sub> alkyl group or a p-nonylphenyl and p is  
3 4.

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FIG. 1A

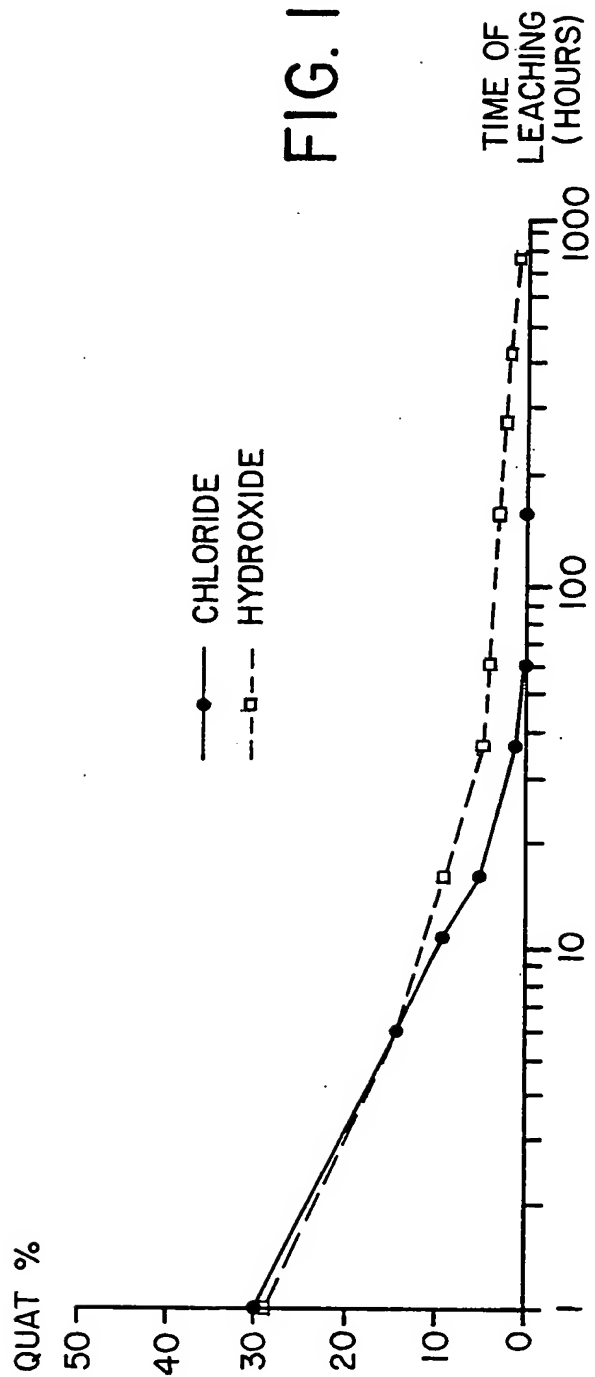
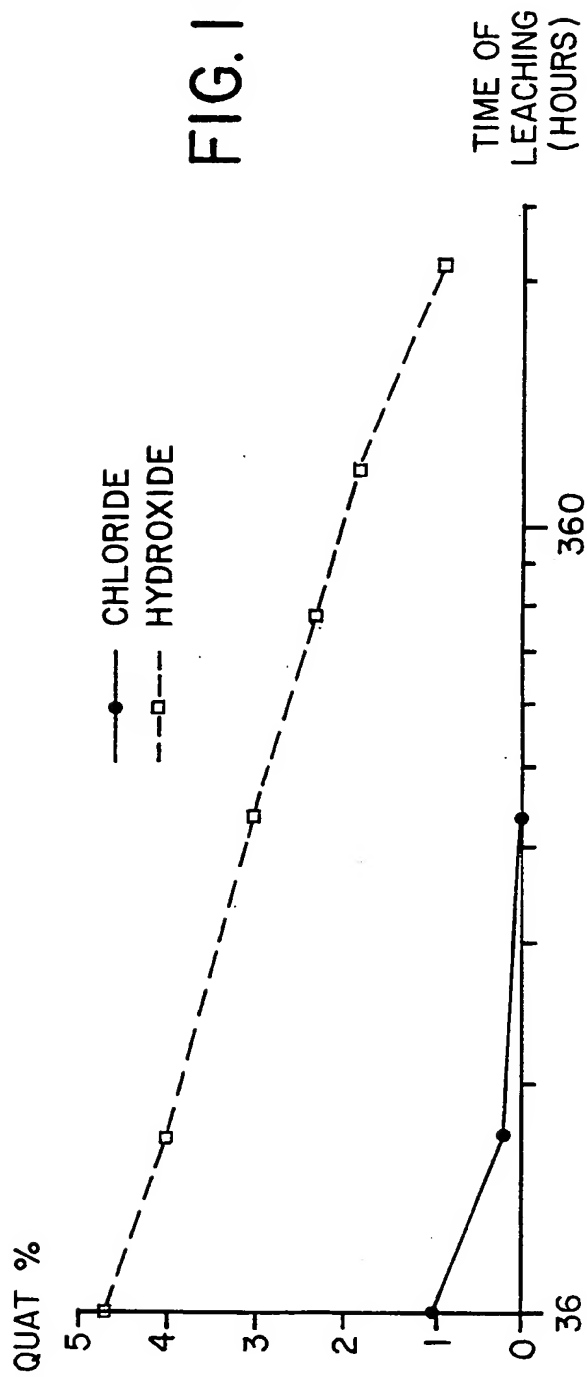


FIG. 1B



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FIG. 2A

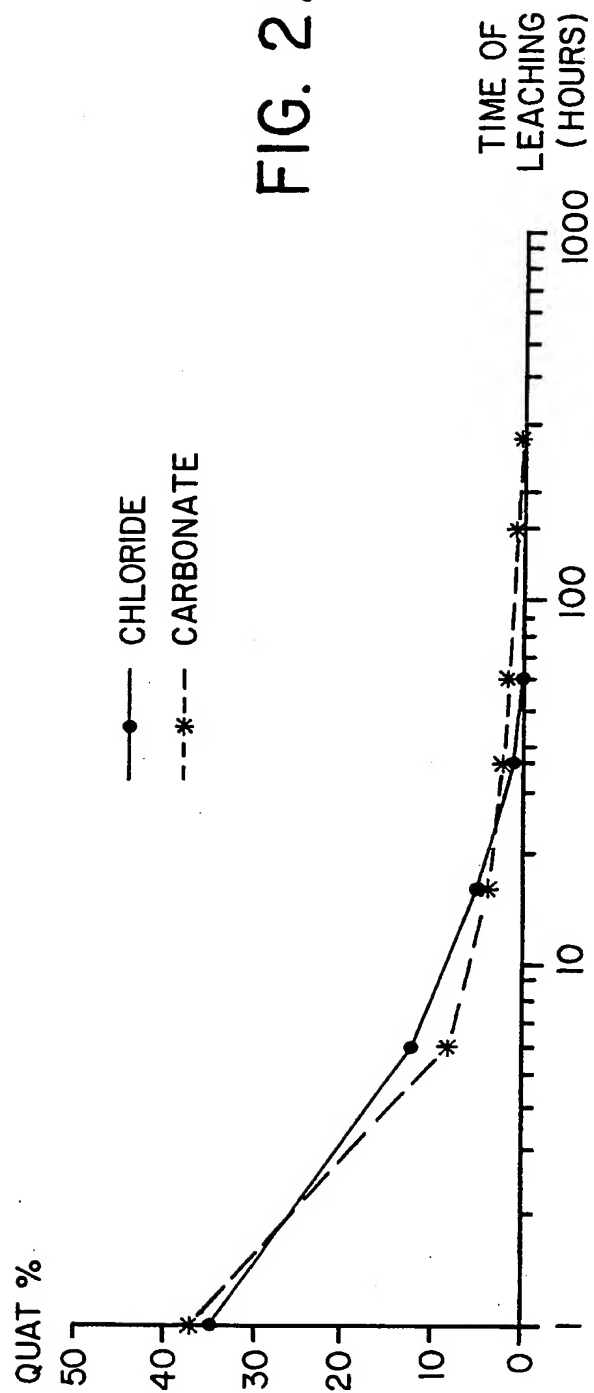
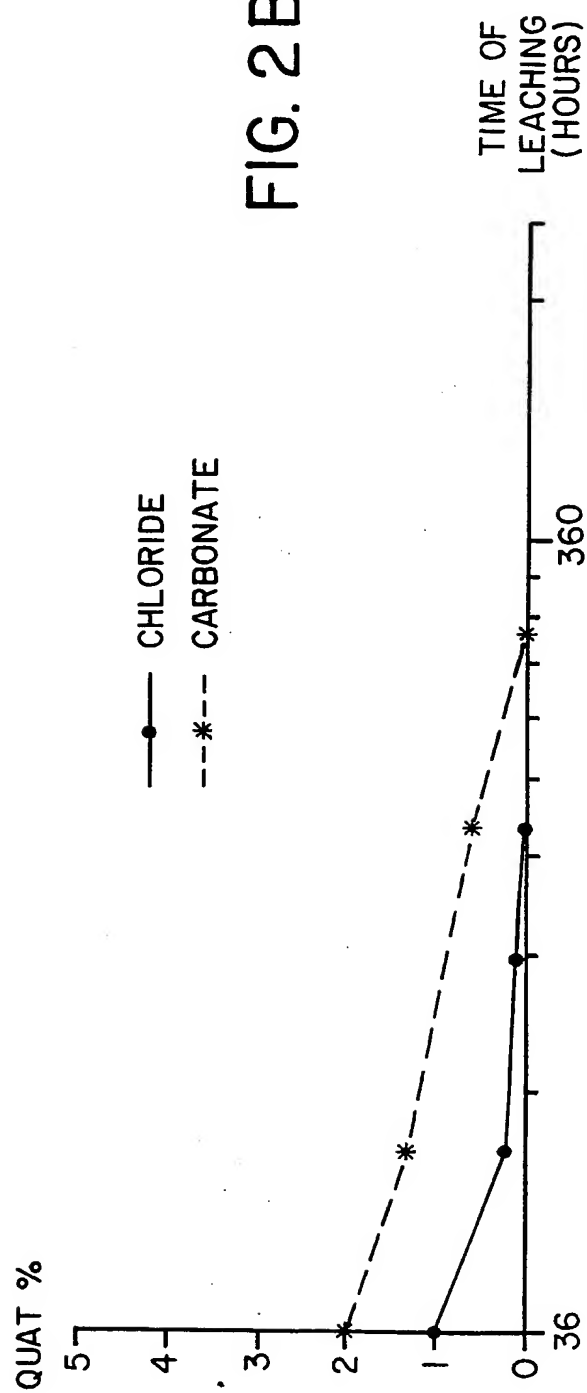


FIG. 2B



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FIG. 3A

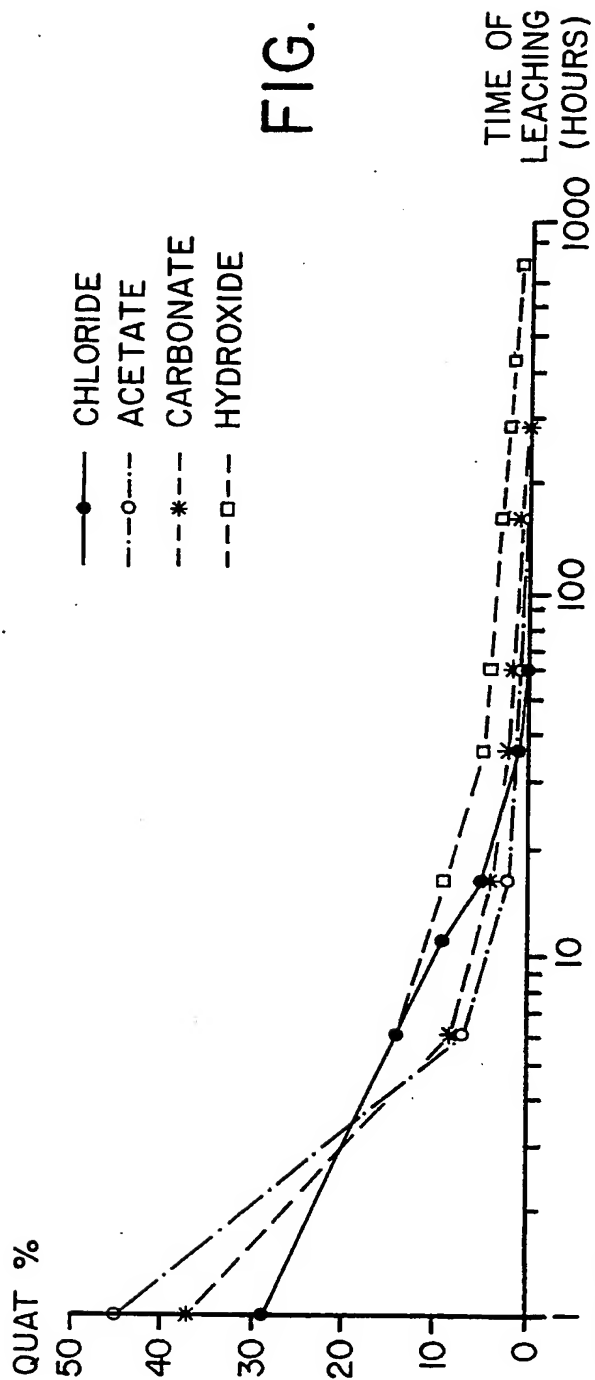


FIG. 3B

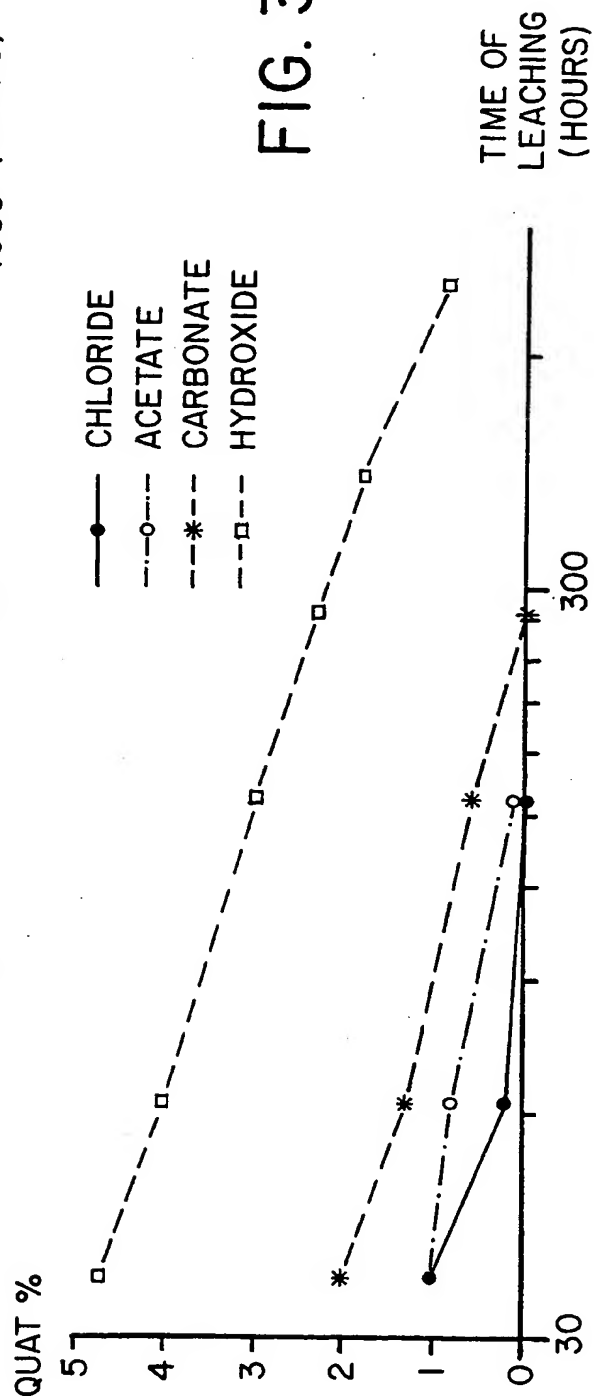
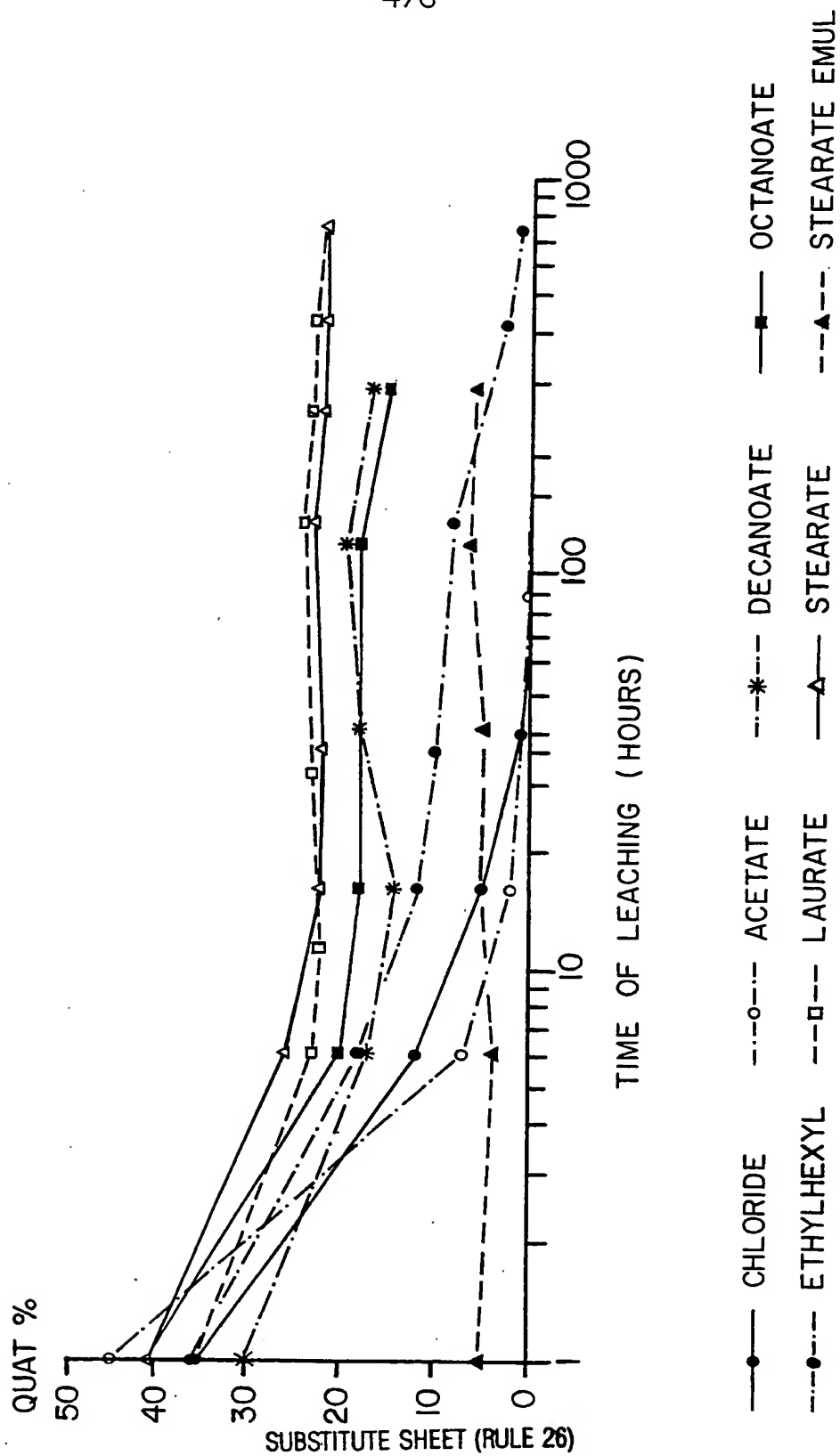
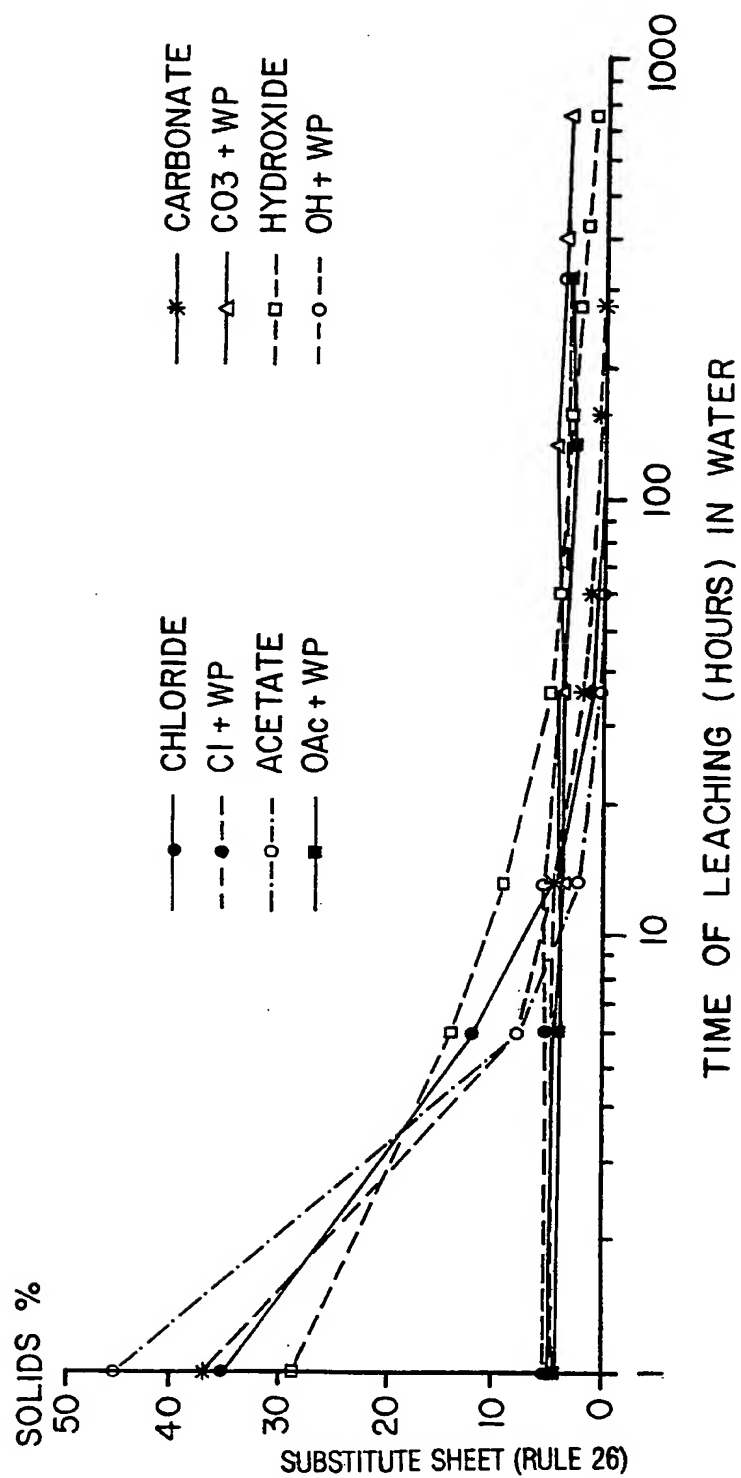


FIG. 3C



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FIG. 4A



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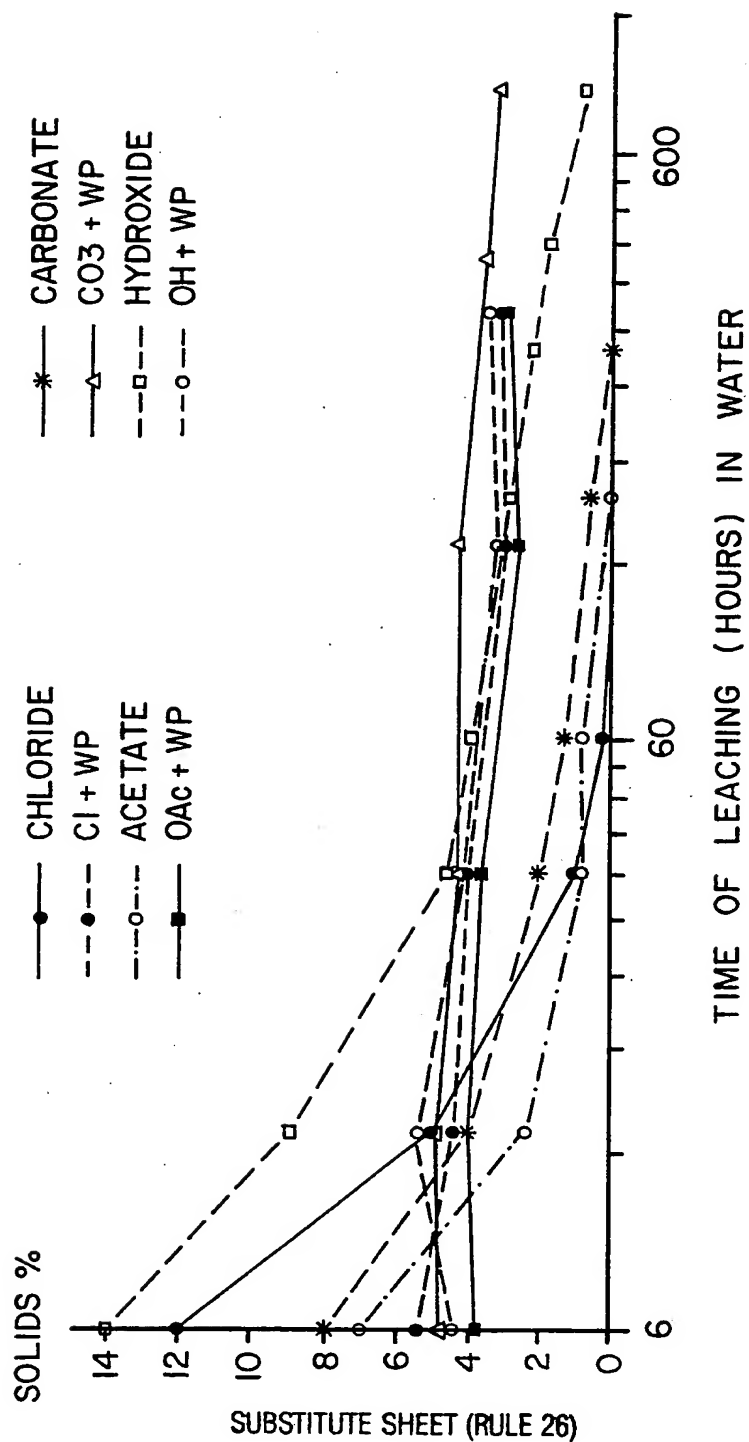


FIG. 4B

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/06699

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAS online: CA, Registry, and CA old files. APS.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,216,168 (Evans et al.) 05 August 1980, see entire document.	1-10, 12-14, 20-21, 25, 29, 34, 35
X -- Y	US, A, 3,169,983 (Hunter) 16 February 1965, see column 1, line 54-column 3, line 63.	9, 10, 12-15, 20-21 ----- 1-15, 36-44
X --- Y	FR, A, 1,518,427 (Bush et al.) 22 March 1968, see claims.	9, 10, 12-14, 20-21 ----- 1-14
Y	Whitten et al. "General Chemistry", published 1981 by Saunders College Publishing (Philadelphia), see page 334.	1-7, 20, 21

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

25 SEPTEMBER 1994

Date of mailing of the international search report

OCT 18 1994

Name and mailing address of the ISA/US  
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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/06699

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	"Fine and Functional Chemicals", Catalogue 91-16, published 1991 by AKZO, see pages 1 and 3-20, especially pages 8 and 9.	1-29, 34, 35-44
X --- Y	US, A, 4,929,454 (Findlay, deceased et al.) 29 May 1990, see entire document.	8-19, 23-29, 33-35 ----- 1-44
Y	Proceedings of the American Wood-Preservers' Association, Vol. 83, issues 1987, Preston et al., "Recent Research on Alkylammonium Compounds in the U.S.", see pages 331-348, see entire document.	1-44
Y, E	US, A, 5,334,763 (Washington et al.) 02 August 1994, see columns 1 and 2.	20-22
X --- Y	EP, A, 0,293,192 (Sexton et al.) 30 November 1988, see entire document.	25-29, 34, 35 ----- 25-35
X	US, A, 4,129,645 (Barnett et al.) 12 December 1978, see illustration I and claim 6.	38, 42
X	US, A, 4,950,329 (McIntyre et al.) 21 August 1990, see column 5, lines 21-26, and the examples.	43, 44
X --- Y	US, A, 5,169,624 (Ziegler et al.) 08 December 1992, see entire document.	36, 37 ----- 36, 37
X	US, A, 3,666,690 (Bann) 30 May 1972, see entire document.	36, 37, 43, 44
X --- Y	Journal of Physical Chemistry, Volume 93, issued 1989, D.D. Miller et al., "Fluorescence Quenching in Double-Chained Surfactants. 1. Theory of Quenching in Micelles and Vesicles", pages 323-333, see page 324, Experimental Section.	25-29, 32-35 ----- 25-35
X --- Y	Journal of the American Chemical Society, Volume 106, issued 1984, J. Brady et al., "Spontaneous Vesicles", pages 4279-80, entire document.	25-29, 34, 35 ----- 25-35
X --- Y	US, A, 3,281,458 (Jordan et al.) 25 October 1966, see entire document.	25-29, 34, 35 ----- 25-35

## INTERNATIONAL SEARCH REPORT

 International application No.  
 PCT/US94/06699

## (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	JP, A, 59-039,337 (Mitsubishi) 03 March 1984, see entire document.	38, 41 ----- 38, 41
X --- Y	EP, A, 0,472,973 (Grunewalder) 04 March 1992, see examples.	43, 44 ----- 43, 44
X --- Y	US, A, 4,545,855 (Sweeney) 08 October 1985, see column 1, lines 6-12 and column 2, lines 48-62 and examples.	36, 37 ----- 36, 37
X	US, A, 4,205,063 (Khalil et al.) 27 May 1980, see examples and column 2, lines 4-12.	38, 41
X --- Y	US, A, 5,045,570 (Mooney et al.) 03 September 1991, see column 4, lines 8-15 and column 5, lines 56-65.	38, 39 ----- 38, 39
X --- Y	Chemical Abstracts, vol. 100, issued 19 March 1984, S. Takemoto et al., "Development of a New Cosmetic O/W, Emulsion System Stabilized With Insoluble Complexes," see abstract No. 91129, J. SCCJ. 17(1), 52-9.	38, 40 ----- 38, 40

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/06699

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/06699

## A. CLASSIFICATION OF SUBJECT MATTER: IPC (5):

A01N 31/14, 33/12, 37/02, 37/06, 37/10, 43/16; B27K 3/00, 3/34, 3/36, 3/38, 3/50, 3/52; C07C 43/13, 43/205, 53/10, 53/122, 53/124, 53/126, 69/67, 69/675, 209/68, 211/63; C07D 309/10; C09K 3/18

## A. CLASSIFICATION OF SUBJECT MATTER: US CL :

106/2, 15.05, 18.32; 252/194, 380, 430; 422/1; 424/405; 428/541; 504/153, 155, 157, 158; 514/473, 546, 547, 549, 552, 557, 558, 560, 642, 643; 549/417; 554/103, 114, 121, 223, 224, 227; 562/606, 607, 608; 564/8, 282, 288, 291, 296; 568/607, 616, 622.

## B. FIELDS SEARCHED

Minimum documentation searched  
Classification System: U.S.

106/2, 15.05, 18.32; 252/194, 380, 430; 422/1; 424/405; 428/541; 504/153, 155, 157, 158; 514/473, 546, 547, 549, 552, 557, 558, 560, 642, 643; 549/417; 554/103, 114, 121, 223, 224, 227; 562/606, 607, 608; 564/8, 282, 288, 291, 296; 568/607, 616, 622.

## BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

Group I, claims 1-15, drawn to quaternary ammonium hydroxide compositions, methods of use, and preparation.

Group II, claims 16-24, drawn to quaternary ammonium carbonate and bicarbonate compositions, methods of use, and preparation.

Group III, claims 25-31 and 33-35, drawn to quaternary ammonium carboxylate or borate compositions, methods of use, and preparation.

Group IV, claims 32, 33 and 35, drawn to an additional method of preparing quaternary ammonium carboxylates differing from that of Group III.

Group V, claims 36 and 37, drawn to waterproofer compositions comprising compounds of formula I.

Group VI, claims 38-42, drawn to waterproofer compositions comprising compounds as shown in claim 38.

Group VII, claims 43 and 44, drawn to waterproofer compositions comprising compounds of the formula X.

The above inventions lack unity under PCT Rules 13.1 and 13.2 in that they lack a single inventive concept — Each grouping corresponds to disparate sets of compounds and compositions.